

# **STUDIES ON LIMITING FLUX PHENOMENA IN ULTRAFILTRATION OF BLACK LIQUOR**

*A Thesis Submitted  
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**MASTER OF TECHNOLOGY**

*by*  
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*to the*  
**DEPARTMENT OF CHEMICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY KANPUR  
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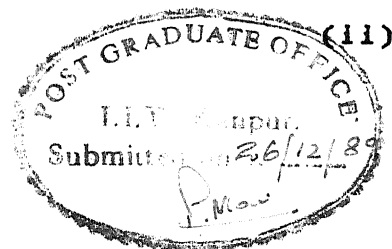
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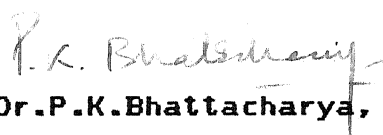
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CERTIFICATE



This is to certify that the work entitled, 'STUDIES ON LIMITING FLUX PHENOMENA IN ULTRAFILTRATION OF BLACK LIQUOR', has been carried out under my supervision and that it has not been submitted elsewhere for a Degree.

December, 1989.

  
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LIST OF SYMBOLS

a,b,c,d	constants in Eqn 5.5	
BL	Black Liquor	
C	solute concentration	(kg/m <sup>3</sup> )
C <sub>p</sub>	concentration of permeate	(kg/m <sup>3</sup> )
D	diffusivity	(m <sup>2</sup> /s)
e	constant in Eqn 3.22	
J	Permeate volumetric flux	(m <sup>3</sup> /m <sup>2</sup> s)
K	membrane coefficient = $1/R_m \mu_w$	(m <sup>3</sup> /Ns)
k	mass transfer coefficient	(m/s)
M	molecular weight	
MF	micro-filtration	
N <sub>Re</sub>	Reynold's number	
P	pressure	(N/m <sup>2</sup> )
PEG	Poly Ethylene Glycol	
r	radius of the membrane	(m)
R	gas constant	
R <sub>m</sub>	membrane resistance	(1/m)
R <sub>o</sub>	observed rejection	
RO	reverse osmosis	
R <sub>p</sub>	polarised layer resistance	
R <sub>r</sub>	real rejection	
T	time	
UF	ultrafiltration	
v	specific volume	(m <sup>3</sup> /kg)
V	volume	(m <sup>3</sup> )

*Greek Letters*

$\alpha, \beta, \gamma$	constants in Eqn.5.1	
$\mu$	viscosity	(kg/ms)
	also chemical potential in Ch.3	
$\omega$	angular velocity	(rad/s)
$\pi$	osmotic pressure	(N/m <sup>2</sup> )
$\rho$	density	(kg/m <sup>3</sup> )
$\nu$	kinematic viscosity	(m <sup>2</sup> /s)
$\Delta$	difference	
$\delta$	membrane thickness	
$\tau$	tortuosity factor	
$\epsilon$	membrane porosity	

*Subscripts*

a	adsorption
appl	applied
b	bulk
eff	effective
i	component
m	membrane surface
p	permeate phase
s	feed solution
uf	ultrafiltration
w	water

*Superscripts*

'	after adsorption
0	standard conditions

ERRATA

- Page 2 , paragraph 2 : please read Gleminius as Glimenius
- Page 3 , paragraph 4 : please read Gleminius as Glimenius
- Page 11, paragraph 1 : please read hydronamics as hydrodynamics
- Page 18, paragraph 2 : please read Nakao *et al* as Wijmans *et al*
- Page 14, Eqn. 3.2 : a is hydraulic-mean pore radius (m).
- Page 47, paragraph 3 : D diameter of stirrer (m)
- N revolutions per second of stirrer.
- Page 9 Jonsson,A.R.,and Auivos,A.,Concentration Polarisation in Reverse Osmosis under Natural Convection ,*Ind. Eng. Chem. Fundam.* ,8(2),359(1969).
- Page 11 Errede,L.A.,Effect of Molecular Adsorption on Water Permeability in Microporous Membranes.,*J. Membrane. Sci.* , 20,45(1984).
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- Page 13 Phillip,A., Aptel,P., Clifton,M.J., and Michaels,A.S., Ultrafiltration,*NATO ASI Ser.* ,*Ser. C.* ,No 181 (Synth.Membr: Sci.Eng.Appl.)249(1986)
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ABSTRACT

Ultrafiltration of Black liquor was carried out using an asymmetric membrane, in a stirred batch cell, modified to work on a continuous mode. Polyethylene Glycol-6000 a standard macromolecule, was used to compare the results. The effects of operating variables viz., differential pressure, bulk concentration and stirrer speed was studied in depth on permeate flux and observed rejection for both the solutes.

Osmotic pressure model was used to analyse the experimental results. Adsorptive resistance was taken into account quantitatively. The polarised layer resistance was found to be a function of membrane surface concentration, applied differential pressure and flow pattern. To relate these, the following correlation was considered and tested with the experimental results.

$$\frac{R_p(F)}{R_m + R_a} = a \left[ \frac{C_m}{\rho_s} \right]^b \left[ \frac{\Delta P_{\text{appl}}}{\Delta \pi} \right]^c \left[ N_{\text{Re}} \right]^d$$

where a, b, c and d are constants.

## CHAPTER-1

### INTRODUCTION

Ultrafiltration (UF) is a rate governed membrane separation process in which pressure is the driving force. It has been gaining prominence as a practical process for concentration and purification of macromolecular and colloidal species in solution. Theoretically and now in practice UF thus offers an attractive alternative to a number of unit operations in food processing, chemical processing, pharmaceutical and medical industries for the concentration, purification and sterilisation of macromolecular and colloidal solutions on both laboratory and industrial scale.

Ultrafiltration avoids many of the deleterious effects of conventional processes associated with phase change, high temperature and denaturing of components. It also serves as a process for additional purification for concentrated products. Glimenius (1980) has presented the observations, viewpoints and the trends on UF for various industries.

Pulp and paper industry is one of the major industries where UF finds extensive applications. It is essential to the economics of the kraft process of pulping that the spent chemicals from the process be recovered, regenerated and reused. The spent chemicals are separated from the pulp at the washing stage along with wood residues, and is called Black Liquor (BL). Black liquor usually contains 98% of the total alkali charged to the digester. The

composition of BL varies considerably in different paper mills, depending on the cooking liquor used and the method of cooking. Most of the alkali in the BL is present as sodium carbonate or as organic sodium compounds very similar in chemical properties to sodium carbonate. The greater part of the organic matter removed from the wood in cooking is combined chemically with sodium hydroxide in the form of sodium salts of resinous and other organic acids. Appreciable amounts of organic sulphur compounds are present in association with sodium sulphite and the rest of alkali is present as free sodium hydroxide and sodium sulphide. There are other impurities too, such as lime, iron-oxide, alumina, potash and sodium chloride.

Black liquor recovery is an integral part of kraft process. The conventional BL regeneration process starts from concentrating the BL (10-15% total dissolved solids) by evaporating the water, then burning in a furnace to separate inorganics and to recover heat. The inorganic ash as smelt is taken up in water, causticized with lime, and reused in the cooking process. Make up sodium and sulphur are added to compensate for losses. The inorganics support combustion and provides steam for process use.

The conventional process requires large capital investment and also destroys the valuable organics portion of BL. Further, dilute BL directly obtained from pulp industries is of the order 100 cubic metre per ton of pulp (Gleminius, 1980) and hence it becomes necessary to recover water. Bigger paper mills have the potential to do so, but smaller mills simply discard the BL. Despite its low concentration from smaller paper mills, disposal of BL is difficult because of high

BOD, colour, toxicity, etc above the standards.

With rising energy costs, increasing capital investments and stricter environmental regulations, it has become more and more important to find efficient and alternative methods to concentrate and fractionate industrial effluents. UF is one such favourable process.

Ultrafiltration finds major applications in pulp and paper industries particularly for the treatment of bleach plant effluents and for spent sulphite liquor (Gleminius, 1980).

Ultrafiltration of black liquor from pulp and paper mills has gained paramount importance not only as a waste treatment but also for recovery of valuable inorganic chemicals and this has become the controlling factor of the economy of the industry. The recovered chemicals are said to be valuable enough to give a short pay-back time for the UF plants.

Gleminius (1980) has reported the following advantages of UF to treat black liquor.

- (i) the liquor is concentrated as much as 25 to 50 times by UF.
- (ii) even a 50% rejection of solids results in atleast a 90% retention of colour.
- (iii) atleast 50% BOD and even more COD is retained.
- (iv) higher molecular weight lignosulphates are retained.
- (v) less energy is consumed.

All the above factors have initiated a resurgency in this area. However, still little attention is being paid to the recovery of chemicals from kraft BL using ultrafiltration.

In earlier works (Mishra and Bhattacharya, 1984; Rajniash and Bhattacharya, 1985; Poddar et al. 1989) attempts were made to analyse the electrodialysive and ultrafiltrative separation of BL. The present work has been undertaken to observe the ultrafiltrative separation of BL and to study the limiting flux phenomena in UF. The work utilises BL as the observing system while a macromolecular solute (PEG-6000) being utilised as a standard solution for comparative analysis. The objectives of the study can be classified as :

(i) to study the effect of independent variables (pressure, concentration, time and flow velocity which are inherent to the system) on dependent variables (permeate flux and observed rejection) for UF of BL and compared to PEG-6000.

(ii) to analyse the factors affecting the concentration polarisation and the resistance of the polarised layer to the flow, utilising an asymmetric membrane.

(iii) to correlate the mass transfer limiting phenomenon with the experimental variables.

## CHAPTER-2

### LITERATURE REVIEW

#### 2.1 Development of membrane:

Membrane separation processes have been in use on a small scale for over a century, but it is only within a period spanning the last three decades that research and development has advanced these processes to commercial significance. The pioneering membranes developed for membrane separation processes were the micro-filtration membranes cast in 1855. Later the first flat membranes were developed in 1872. However, the development of membranes and studies on membrane properties did not catch up until and after the World War II. Up to the sixties the membranes were classified as tortuous or sponge like until the advent of Nuclepore membranes from the General Electric Corporation, which revolutionised over the cellulosic membranes. These membranes were thinner, less porous and more flexible. The study of structure and shape of the membranes was made possible due to the invention of electron microscope.

Early studies to reduce the porosity were highly empirical. Researchers were studying the effects of concentration of membrane substance in casting, drying time required, solvent ratio, additives, etc. In 1957 it was found that cellulose acetate had the greatest permeability and rejection.

(Kesting.,1977).The development of an excellent hypothesis which could accomodate every class of membrane initiated the art of casting membranes.

Contemporarily Loeb and Sourirajan (1958,1959,1960,1961) developed a new technique to cast Reverse Osmosis(RO) and Ultra Filtration(UF) membranes.These were able to reduce the resistance to the flow without affecting the other characteristics of the membranes.These membranes were integrally skinned anisotropic membranes and they initiated both commercial and academic interest,intitially in desalination and subsequently in various other membranes processes.

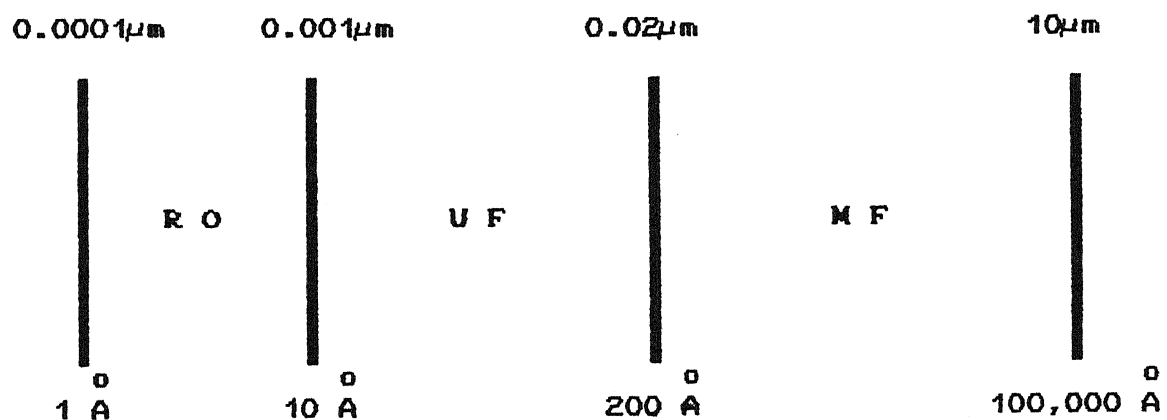
In an attempt to increase the active membrane surface area the hollow fiber membranes came into existence.DuPont and Dow Chemical developed a variety of such hollow fiber membranes.More recently (Rozelle et al.,1975) composite membranes heve been developed.These are structurally similar to Loeb-Sourirajan membranes,but nevertheless they provide a free hand in tailoring various characteristics of membranes.

Details about History and Development of membranes are discussed (Kesting.,1977;Schweitzer.,1974).

## 2.2 Ultrafiltration:

Ultratfiltration (UF) through semi-permeable membranes has been recently evaluated as a most promising method for seperation,purification,fractionation and concentration of substances like proteins and other macromolecules.This falls under the category of pressure driven membrane separation processes.There is considerable dispute as to the distinction

between Reverse Osmosis, Ultra Filtration and Micro Filtration (MF). The most useful definition of these processes is based on the smallest particle or molecule retained by the membrane. According to Porter (1975, 1977), the processes are defined by the rated pore size or the molecular-weight cut-off of the membranes as follows:



The characteristic features of this process (Drioli., 1978) are following:

- (i) It is athermal and can be carried out at constant temperature when necessary.
- (ii) No phase change is required.
- (iii) The operation needs low hydraulic pressure.
- (iv) The molecules are not denatured.



- (v) Chemical agents are not required generally.
- (vi) The process is economical.
- (vii) Ionic strength and  $p^H$  of the concentrate are maintained constant.

In UF the dispersed phase (i.e., solute) passes less readily through the membrane than the solvent. The reasons attributed for this may be classified as (Ferry., 1936; Tuwiler., 1962):

- (i) The solute may be adsorbed on the surface of the filter and its pores (primary adsorption).
- (ii) The solute may be retained within the pores (blocking).
- (iii) It may be mechanically retained (sieving).

One of the problems found in UF is a marked decline of the permeate flux with time. Albeit the rejection achieved could be quite high for even salts, the flux was too low to be of any practical utility.. This is mostly attributed to the deposition of a concentrated layer of macro-solute molecules at the membrane-solution interface; the layer acting as additional barrier to the flux of the solvent and micro solutes. This build up of retained solutes and particles on the membrane acts as a dynamic membrane which becomes the limiting resistance to the flow and offers a higher retention capability than the support itself. Blocking and primary adsorption may also synergate.

These phenomena have led to the coining of phrases "Concentration Polarisation" (Michaels., 1968)—a concentrated boundary layer formed at the membrane surface, which reduces the flux—and "Fouling"—the irreversible attachment of solute on the

membrane. Concentration polarisation may be considered reversible including reversible deposition. This reversible deposition or reversible fouling may not be isolated (Aimar, 1988). A prolonged concentration polarised UF plant may lead to fouling phenomena. The primary factors for these two phenomena are the concentration of the feed, operating differential pressure across the membrane, velocity of the feed and temperature. Various secondary factors like the residual charge on the membrane, ionic strength of the feed, etc., are also found to affect.

The literature available in concentration polarisation is vast and varied and dates back to 1966. Gill (1966) has done pioneering work starting with RO desalination. This was followed by Jonsson (1969) who tried to quantify concentration polarisation from the governing laminar boundary natural convection solutions. Goldsmith (1971) used geometric properties of the membrane pores and macromolecules in the solution to quantify retention and mass transfer. Kozinsky and Lightfoot (1972) developed a model for a special case of UF through a rotating disk.

Thomas (1973) concluded that in terms of a simple eddy diffusion model boundary layer decreases with Schmidt number. Kozinsky *et al.* (1974) also attempted a similarity solution and found that concentration polarisation was essentially independent of suction velocity distribution. Porter (1972) and Shen *et al.* (1977) combined the effects of mass transfer by diffusion and formation of filter cake and concluded both to be interactive with each other. Bellucci *et al.* (1975) and Swaminathan (1978) showed the results of

protein UF considering gel polarisation model. Jonsson *et al.* (1977) concluded the transition from laminar to turbulent region was in the range Reynolds No. 1000 to 2500 in a parallel plate channel. An integral solution for the limiting case of linear osmotic pressure was obtained (Probstein, 1979). Jonsson (1980) has outlined the applicability of various models for the transport of water and solute in UF/RO membranes. Quantitative models for membrane fouling have also been reported by Green *et al.* (1980).

The results of solute mass balance solved by an integral method were shown to contradict the film theory model (Trettin *et al.*, 1980; 1981) (the film theory model supports that the permeate flux varies logarithmically with solute concentration.).

Modelling for colloidal fouling was developed by Schippers *et al.* (1981). This was based upon the cake or gel filtration theory. It was suggested that at the initial period of UF blocking filtration may take place instead of gel filtration.

While in these experiments the anisotropic membrane was considered to have a uniformly distributed permeability, Fane *et al.* (1981) took regions of differing permeability into consideration for analysis. The gel polarised UF membrane was viewed as a physical analogue of a composite RO membrane. This gel polarised UF was said to depend on membrane permeability and surface properties. A correction factor was introduced for the available free area by them.

The effect of secondary factors like solute size, solute hydrophobicity,  $p^H$  and the ionic strength of the feed, etc., was studied by Zeman (1983). Multiple solute UF was found to show different

results compared to single solute UF on the time of adsorption .

The influence of solute properties and membrane surface characteristics on adsorption kinetics and hydromatics shows atleast two distinct controlling steps of adsorption (Mathiasson,1983).A strong variation of transmembrane pressure was modelled to quantify the degree of fouling (Flemmer,1983).Buckley (1983) developed a model to predict flux decline before and after the onset of gel polarisation.

A summary of the concept of concentration polarisation,limitations and the ways to reduce concentration polarisation,membrane fouling, solute membrane interactions etc.have been discussed in detail (Belfort *et al.*1983).

The dynamics of polarisation in stirred and unstirred UF was studied by Chudacek *et al.*(1984).The simple Carman-Kozeny equation was shown to be a good approximation to the amount of solute in the polarised layer.Filtration theory was utilised to evaluate the specific resistance.Marked affection of water permeation and permeability due to adsorption of hydrocarbon impurities and trace inorganic ions also affects concentration polarisation and fouling (Errede,1984).

Wijmans *et al.*(1984,1985) have explained the flux limitations in UF in terms of osmotic pressure. On the other hand Jonsson (1984) suggests that a degree of osmotic limitation has to be considered along with gel polarisation model.Dickson *et al.*(1984) and Do *et al.*(1984) have also discussed in this line.The limiting flux is independent of applied pressure and is strongly

dependent on stirred and bulk concentration.

Shu-Sen Wang *et al.* (1985) have used least squares approximation to determine the rate constant of gel growth. By defining the concentration profiles in the boundary layer they have modelled to determine the period of cleaning of the membrane surface. By utilising permeability data from sedimentation experiments, Wijmans *et al.* (1985) have showed that osmotic pressure model and the boundary layer resistance model are equivalent.

There is a particular interest in UF of Bovine Serum Albumin (BSA) and Poly Acrylic Acid (PAA). On these systems, Choe *et al.* (1986) have conducted batch UF experiments. It was concluded that the polymer chain flexibility affects the fouling to a great extent.  $p^H$  and ionic concentration affects the fouling of PAA but does not affect fouling of BSA. They also suggest that while for PAA the fouling is mainly due to pore plugging, BSA fouling is due to solute-membrane interaction. The same result was obtained by Aimar *et al.* (1986). Adsorption of BSA was reported to follow Freundlich law. It was also reported that drastic changes in the filtration property of BSA due to solute-membrane interaction. By assuming the polarised layer to be less porous and highly resistive to the flow, Suki *et al.* (1986) have derived a model. This model is derived from flocculation theory and it shows a high solute-membrane interaction.

Nakao *et al.* (1981, 1986) considered cake filtration theory to analyse concentration polarisation and fouling in unstirred conditions. This was followed soon by Aimar *et al.* (1986, 1988). In the later work they have put forward four models for evaluating

concentration polarisation. The convective deposition with constant removal of flux developed by them matches closely with their experimental results. A model based on adsorption isotherm and another on gel-layer growth have also been derived and discussed.

There are a few literature review papers available for the mass transfer phenomena in UF. Of these Gekas *et al.* (1987) presents a detailed discussion on factors like porosity, wall roughness, change in viscosity and diffusion coefficient. Gill (1988) has discussed the effect of viscosity on fouling and mass transfer using an integral model. The optimal operating conditions to be chosen are discussed in detail, although there is a defect in the model due to the assumption of constancy in permeate flux. More extensive reviews are also available (Porter *et al.*, 1986; Phillip *et al.*, 1986; Muhammed, 1982; Belfort, 1984; Mazid, 1988).

### CHAPTER-3

#### THEORETICAL CONSIDERATIONS

##### 3.1 Flux through the membrane:

In the absence of a solute, the flux,  $J_w$ , through a porous membrane is defined by Darcy's law, which states that the pure solvent flux is directly proportional to the applied pressure differential,  $\Delta P_{\text{appl}}$ , and inversely proportional to the pure solvent viscosity,  $\mu_w$ , (Nguyen et al., 1979):

$$J_w = K \Delta P_{\text{appl}} ; K = \frac{1}{R_m \mu_w} \quad (3.1)$$

where  $R_m$ , is the membrane intrinsic hydraulic resistance. It is a function of pore size, tortuosity, membrane thickness and porosity as follows:

$$R_m = \frac{8\tau\delta}{\epsilon a^2} \quad (3.2)$$

Since UF membranes are plastic and can yield (compact) under pressure,  $R_m$  is also a function of the pressure history. Initial membrane compaction occurs rapidly during start-up, whereas long term compaction occurs slowly over the operating life of the membrane (Klinkowski, 1984). However, improvements made with thin-film composite membranes lessen this effect.

Equation 3.1 no longer holds true when the solution contains retained solutes. This flux ( $J_{uf}$ ) in an ultrafiltration run is

generally lower than the pure solvent flux in absence of solute  $J_w$ , and this is also decreasing with time. For example Fig. 3.1 shows the variations of flux,  $J$ , versus the applied pressure differential  $\Delta P_{appl}$ , for an UF run.

In Fig 3.1 curve 'a' represents Darcy's law for the pure solvent ( $J_w$ ), while curve 'b' represents the actual experimental UF flux ( $J_{uf}$ ). From the figure it can also be noted that the slope of  $J_{uf}$  is less than that of Darcy's law, while at higher pressures the flux,  $J_{uf}$ , becomes asymptotic to X-axis, thereby implying to be independent of applied pressure. It may be further said that point 'c' is time dependent while point 'd' is time independent. These points 'c' and 'd' may be drawn as a function of time as on Fig. 3.2

If after an UF run the membrane is thoroughly washed with appropriate washing solution and the solvent flux ( $J'_w$ ) is determined under the same applied pressure  $\Delta P_{appl}$ , it may be found to be less than  $J_w$ , but still greater than  $J_{uf}$ . The difference between  $J_w$  and  $J'_w$  is accounted for the irreversible fouling of the membrane due to the attachment of matter on the surface and inside the pores of membranes. This loss of flux can be visualised as additional resistance to the flux,  $R_a$ . Hence

$$J'_w = \frac{\Delta P_{appl}}{\mu_w (R_m + R_a)} \quad (3.3)$$

The difference between  $J_{uf}$  and  $J'_w$  arises from a phenomenon which disappears when the UF pressure is released or when the membrane is rinsed. There are two different types of phenomena that



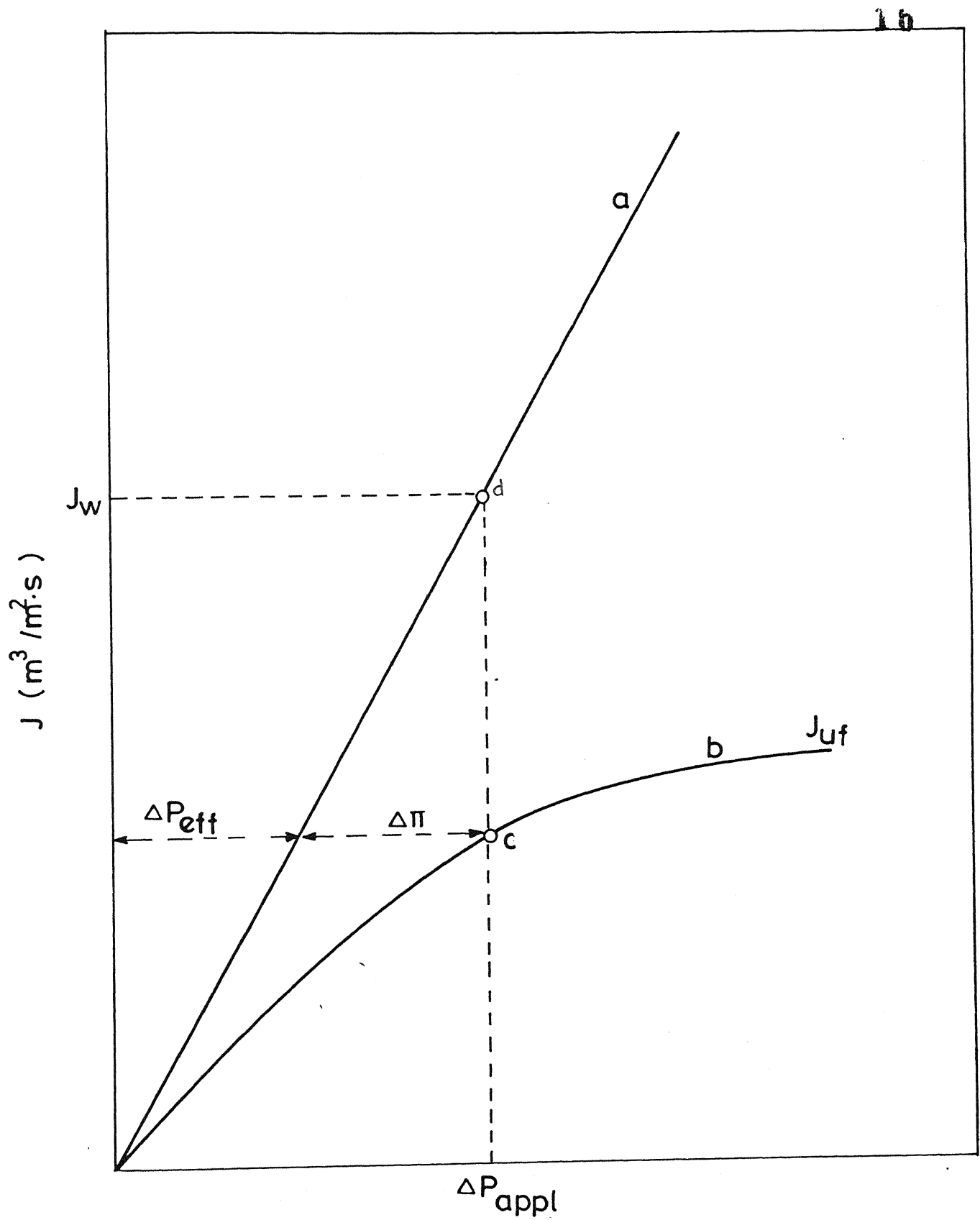


Fig.3.1 Variation of permeate flux as a function of applied pressure (Aimar et.al.,1988)

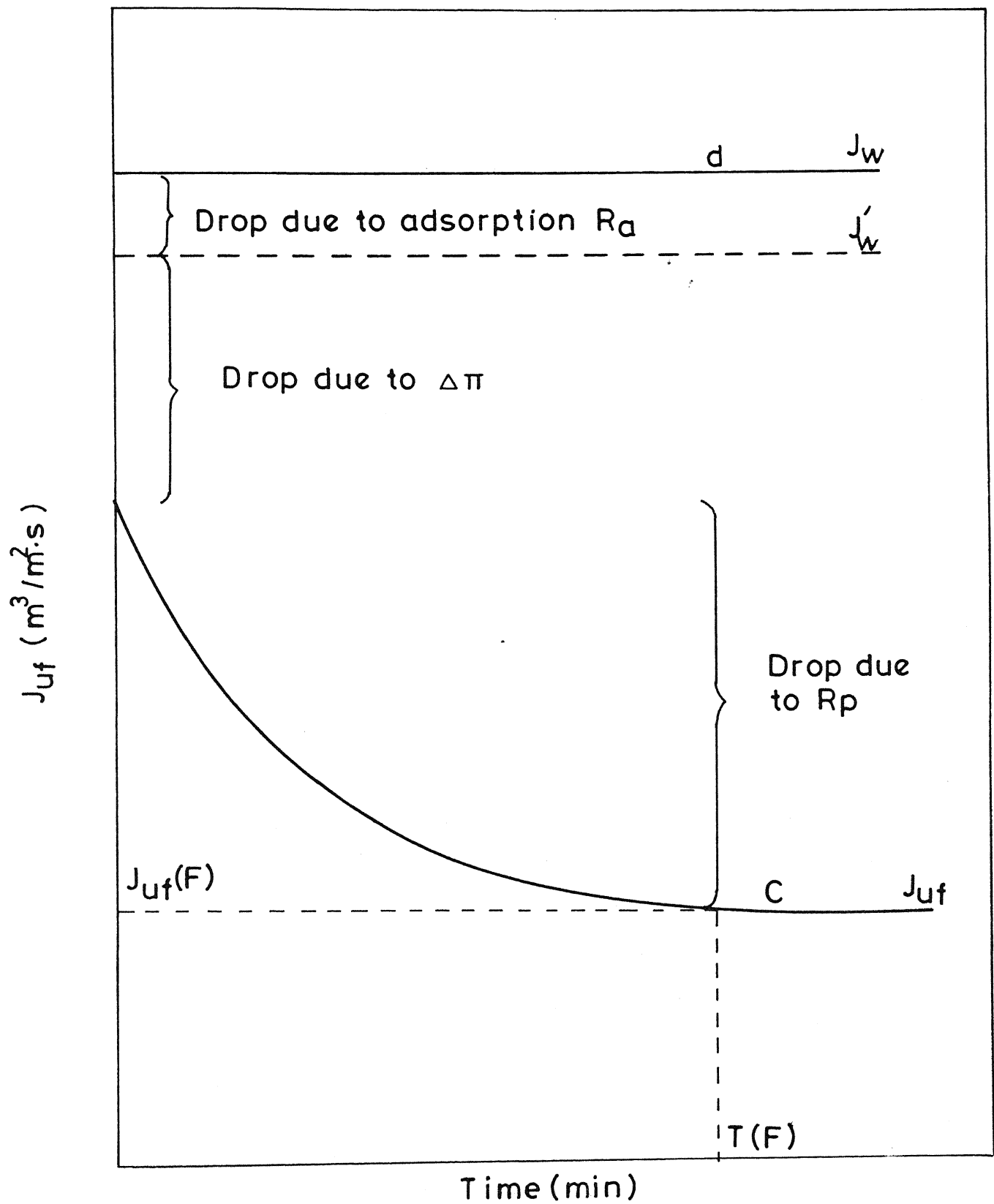


Fig.3.2 A graphical illustration of the possible ways for the drop in permeate flux

may explain this:

- (i) the osmotic pressure model says a negative and reversible osmotic pressure is developed (Clifton et al., 1984; Vilker et al., 1981), or
- (ii) as per the gel-polarisation model a depositive layer resistive to the flow is said to be formed which is reversible in nature.

It has been impossible until now to distinguish these two phenomena, which get modified as soon as the UF mass transfer is changed in any manner. As a consequence all these phenomena may be characterized as if they reduce the applied pressure  $\Delta P_{\text{appl}}$ , by an equivalent osmotic pressure,  $\Delta \Pi$ , down to an effective pressure,  $\Delta P_{\text{eff}}$ , defined as (Aimar, 1988):

$$\Delta P_{\text{eff}} = \Delta P_{\text{appl}} - \Delta \Pi \quad (3.4)$$

In recent times Nakao et al. (1985) have showed that both the above models are equivalent to each other, while Jonsson (1984) suggests that a degree of osmotic limitation along with gel-polarisation to be considered. The above two models may be theoretically represented as follows:

$$J_{\text{uf}} = \frac{\Delta P_{\text{appl}} - \Delta \Pi}{\mu_s (R_m + R_p + R_a)} \quad (3.5)$$

where  $\mu_s$  is the viscosity of the feed solution and  $\Delta \Pi$  is the osmotic pressure difference between the feed and the permeate membrane surface concentrations.

Experimentally  $R_m$  and  $R_a$  could be obtained by measuring pure

solvent flux  $J_w$  and  $J'_w$  from Eqns.3.1 and 3.3.

The time dependent case of Eqn 3.5 can be modified as:

$$J_{uf}(t) = \frac{\Delta P_{appl} - \Delta \Pi}{\mu_s [R_m + R_p(t) + R_a]} \quad (3.6)$$

From Fig.3.2 it should also be noted that  $J_{uf}$  reaches an almost constant final flux  $J_{uf}(F)$ . The time corresponding to this  $J_{uf}(F)$  is  $T(F)$ . This factor implies that at  $J_{uf}(F)$ ,  $R_p(t)$  becomes constant,  $R_p(F)$ . Hence, Eqn.3.6 may be modified at this final level as:

$$J_{uf}(F) = \frac{\Delta P_{appl} - \Delta \Pi}{\mu_s [R_m + R_p(F) + R_a]} \quad (3.7)$$

### 3.2 Concentration polarisation:

In membrane separation processes a phenomenon called concentration polarisation always exists, due to which the concentration at the membrane solution interface is always higher than the bulk solution concentration. This phenomena may be mathematically modelled by writing the solute mass balance for an infinitesimal element in the boundary layer and further integrating the following with the appropriate boundary conditions:

$$J C - J C_p = \left[ -D \frac{dC}{dx} \right] \quad (3.8)$$

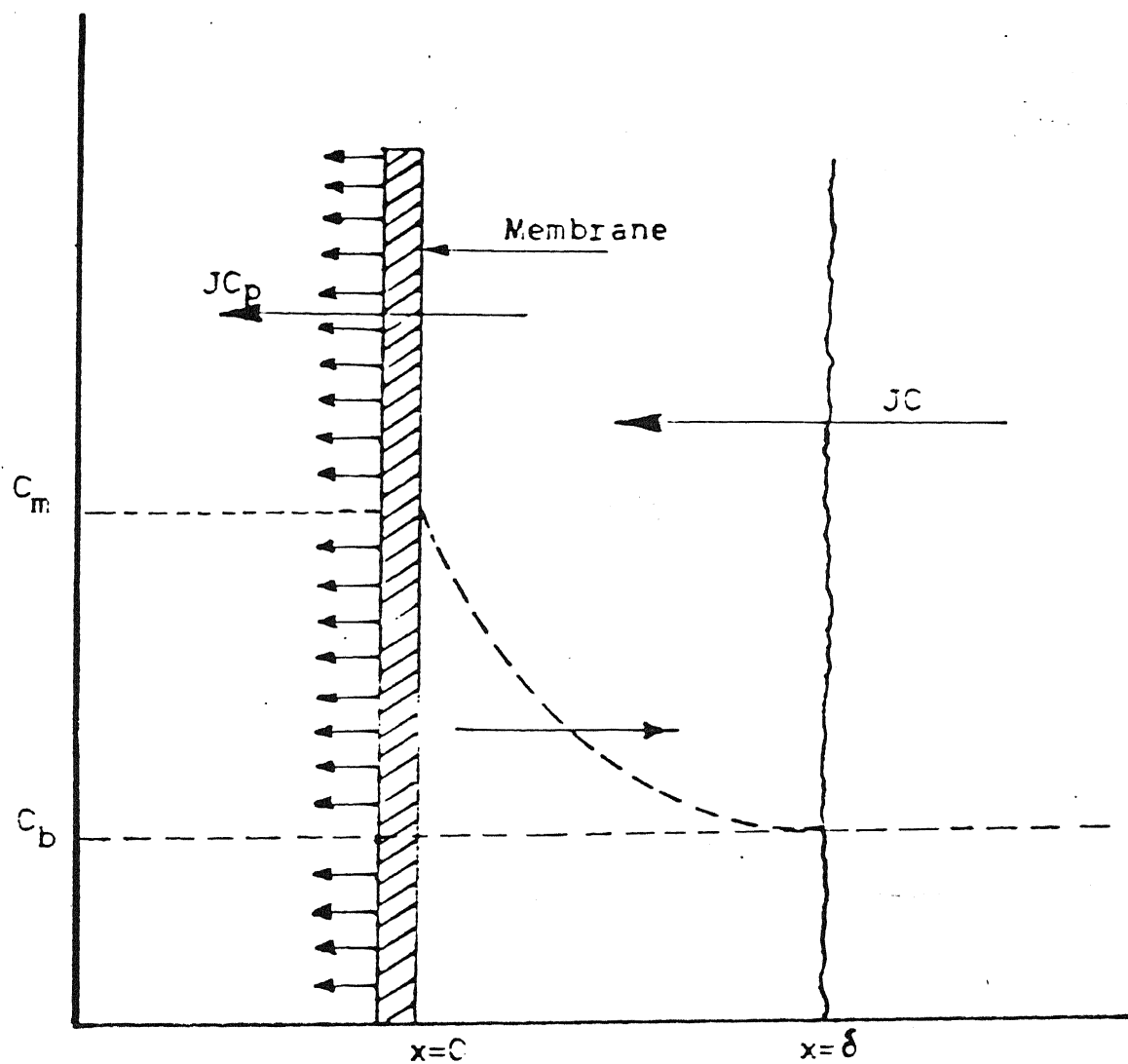


Fig.3.3 Concentration Polarization at Steady State.

On integration we obtain:

$$J = k \ln \left[ \frac{C_m - C_p}{C_b - C_p} \right] \quad (3.9)$$

where  $k = \frac{D}{\delta}$  is the mass transfer coefficient.

For a stirred batch cell the mass transfer coefficient can be found by the following empirical correlation (Sherwood, T.K., 1975).

$$k = 0.0443 \left[ \frac{D}{r} \right] \left[ \frac{\nu}{D} \right]^{0.33} \left[ \frac{\omega r^2}{\nu} \right]^{0.8} \quad (3.10)$$

where,  $r$  = radius of the membrane (cm),

$\nu$  = kinematic viscosity of the feed solution (St),

$\omega$  = angular velocity (rad/s) and

$D$  = diffusivity (cm<sup>2</sup>/s).

Further the diffusivity has been related empirically to molecular weight of polymeric solutions (Sherwood, T.K., 1975) as follows:

$$D = 2.74 \times 10^{-5} (M)^{-1/3} \quad (3.11)$$

### 3.3 Osmotic pressure model and Flory's equation:

Because of the concentration polarisation phenomena, the concentration at the membrane solution interface is always higher than that at the bulk. Due to this a negative osmotic pressure is developed which acts against the applied pressure. Hence the effective pressure differential is less than the applied pressure (Eqn. 3.4). In osmotic pressure model, this effective pressure differential is used to calculate  $J$  as follows:

$$J = \frac{\Delta P_{\text{appl}} - \Delta \Pi}{\mu_s \left( R_m + R_a \right)} \quad (3.12)$$

Here  $\Delta \Pi$  is the osmotic pressure difference between the membrane solution interface at the concentrate and permeate sides respectively.

The osmotic pressure depends on the concentration and the molecular weight of the solute. From thermodynamics we can say at osmotic equilibrium the chemical potential of the solvent must have the same value on each of the membrane. Hence

$$\frac{\Pi}{RT} = - \frac{(\mu_i - \mu_i^0)}{V_1 RT} \quad (3.13)$$

where  $\mu_i$  is the chemical potential of the solvent in solution,  $\mu_i^0$  is the chemical potential of pure solvent at the same temperature.

We can express the chemical potential  $\mu_i$  as follows (Flory., 1953).

$$\mu_i - \mu_i^0 = RT \left[ \ln \gamma_1 + \left( 1 - \frac{1}{X} \right) \gamma_2 + X_1 \gamma_2^2 \right] \quad (3.14)$$

From Eqns. 3.13 and 3.14

$$\Pi = - \frac{RT}{V_1} \left[ \ln \gamma_1 + \left( 1 - \frac{1}{X} \right) \gamma_2 + X_1 \gamma_2^2 \right] \quad (3.15)$$

where 
$$X = \frac{\text{volume of polymer molecule}}{\text{volume of solvent molecule}}$$

$$= \frac{v_p M / N_{av}}{V_1 / N_{av}}$$

$$= \frac{v_p M}{V_1} \quad (3.16)$$

Here  $V_1$  is the molar volume of the solvent,  $v_p$  is the specific volume of polymer, and  $M$  is the molecular weight of the solvent. Eqn. 3.16 can also be written as

$$X = \frac{v_p M}{v_1 M_1} \quad (3.17)$$

where  $v_1$  is the specific volume of solvent and  $M_1$  is the molecular weight of solvent.

$\gamma_1$  and  $\gamma_2$  of Eqn. 3.14 depend strongly on concentration and can be expressed as:

$$\gamma_2 = C v_p = C / \rho_p \quad (3.18)$$

where  $C$  is the concentration,  $\rho_p$  is the density of the polymer at the amorphous state ( $= 1.125 \text{ gm/cc}$ ) (Vankrevelen., 1972), and

$$\gamma_1 = 1 - \gamma_2 \quad (3.19)$$

$$X_1 = 0.45 \text{ for PEG-water system (Vankrevelen., 1972).}$$

So one can calculate the osmotic pressure from Eqns. 3.14 through 3.19.



### 3.4 Observed and Real Rejection:

Rejection is a measure of the ability of the membrane to retain a particular solute. Two types of rejection are generally used to describe the characteristics of a membrane, namely the observed and the real rejections.

The observed rejection is expressed as

$$R_o = 1 - C_p / C_b \quad (3.20)$$

where  $C_p$  is the permeate concentration and  $C_b$  is the bulk concentration. But due to the concentration polarisation the membrane solution interface concentration is higher than that at the bulk. So the real rejection is

$$R_r = 1 - C_p / C_m \quad (3.21)$$

where  $C_m$  is the membrane surface concentration.

### 3.5 Velocity variation technique:

Mass transfer coefficient ( $k$ ) can be determined by using velocity variation technique (Nakao *et al.*, 1981), for a solute of unknown physical properties. From Eqn. 3.10, it is known at any constant concentration,  $k$  is proportional to the stirrer speed ( $\omega$ ). So we can write,

$$k = e (\omega)^{0.8} \quad ; e \text{ is a constant} \quad (3.22)$$

Using Eqns. 3.20 and 3.21, Eqn. 3.9 can be expressed as

$$\ln \left[ \frac{1 - R_o}{R_o} \right] = \ln \left[ \frac{1 - R_r}{R_r} \right] + \left[ \frac{J}{k} \right] \quad (3.23)$$

Substituting eqn.3.22 into Eqn.3.23,

$$\ln \left( \frac{1 - R_o}{R_o} \right) = \ln \left( \frac{1 - R_r}{R_r} \right) + 1/e \left( \frac{J}{\omega^{0.8}} \right)$$

Equation 3.24 is a straight line plot of  $\ln \left( \frac{1-R_o}{R_o} \right)$  (3.24)

versus  $(J/\omega^{0.8})$ . The value of  $e$  and therefore mass transfer coefficient can be found from the slope of this plot.

CHAPTER-4EXPERIMENTAL WORK4.1 Instruments and Materials:4.1.1 Membrane:

Type	Spectra/Por ; C5 SPECTRUM® Medical Industries Inc,U.S.A.
Nature	Flat disc,asymmetric, anisotropic and hydrophillic.
Diameter	76 mm.
M.W.C.D.	5000,sharp.
Composition	cellulose acetate material or hydrolised cellulose acetate.
p <sup>H</sup> range	2 to 10.
Maximum temperature	90°C.
Support	highly porous,150 to 300 µm.
Skin	0.1 to 0.5 µm.
Sterilisation	by formalin or hydrogen peroxide or ethylene oxide.
Suggested cleaning	by detergent with enzymes or 2.5% hydrogen peroxide.
Storage	1 to 2 % formaldehyde.

4.1.2 Stirrer:

Diameter of the

stirrer

56 mm.

Height of the stirrer

above the membrane

30 mm.

4.1.3 Stirrer motor:

Type

shunt, continuous rating.

Supply

220V, DC.

Horse power

0.125 HP.

rpm

1450.

Amperage

0.85 A.

4.1.4 Pump:

Type

reciprocating.

Supply

220V, 1Ph, 50Hz.

Amperage

2.6A.

rpm

1425.

Wattage

180W.

4.1.6 Stroboscope:

Type

1531-A

General Radio Company,

U.S.A.

Range

110 to 690.

rpm per division

5

#### 4.1.7a Refractometer:

Model	Pzo, Warsaw, RL1, Poland.	
Range of measuring scale	1.3 to 1.7	
Accuracy	0.0002	$1.30 < R.I < 1.42$
	0.0004	$1.42 < R.I < 1.70$

#### 4.1.7b Weighing balance:

Model	Saratorius, 2004MP.
Accuracy	0.00001g
Maximum weight	166.0g

### 4.2 Experimental device:

#### 4.2.1 Apparatus:

The main aim of the experiments were to examine the factors affecting the decrease in flux with respect to time. So it was necessary to conduct the experiments on a continuous mode and at steady state. Since the experiments were conducted using a batch cell ultrafilter the permeate had to be pumped back into the cell to maintain the bulk concentration constant. This would enable to conduct the experiment at steady state.

In practice to recycle the permeate and thereby maintain the bulk concentration constant was achieved using a high pressure metering pump. The metering pump itself was used to pressurise the system, thereby eliminating the need of a compressor or compressed nitrogen. The experimental set-up is shown in Fig.4.1.

The specifications of the cell (Fig.4.2), designed and fabricated were as follows:

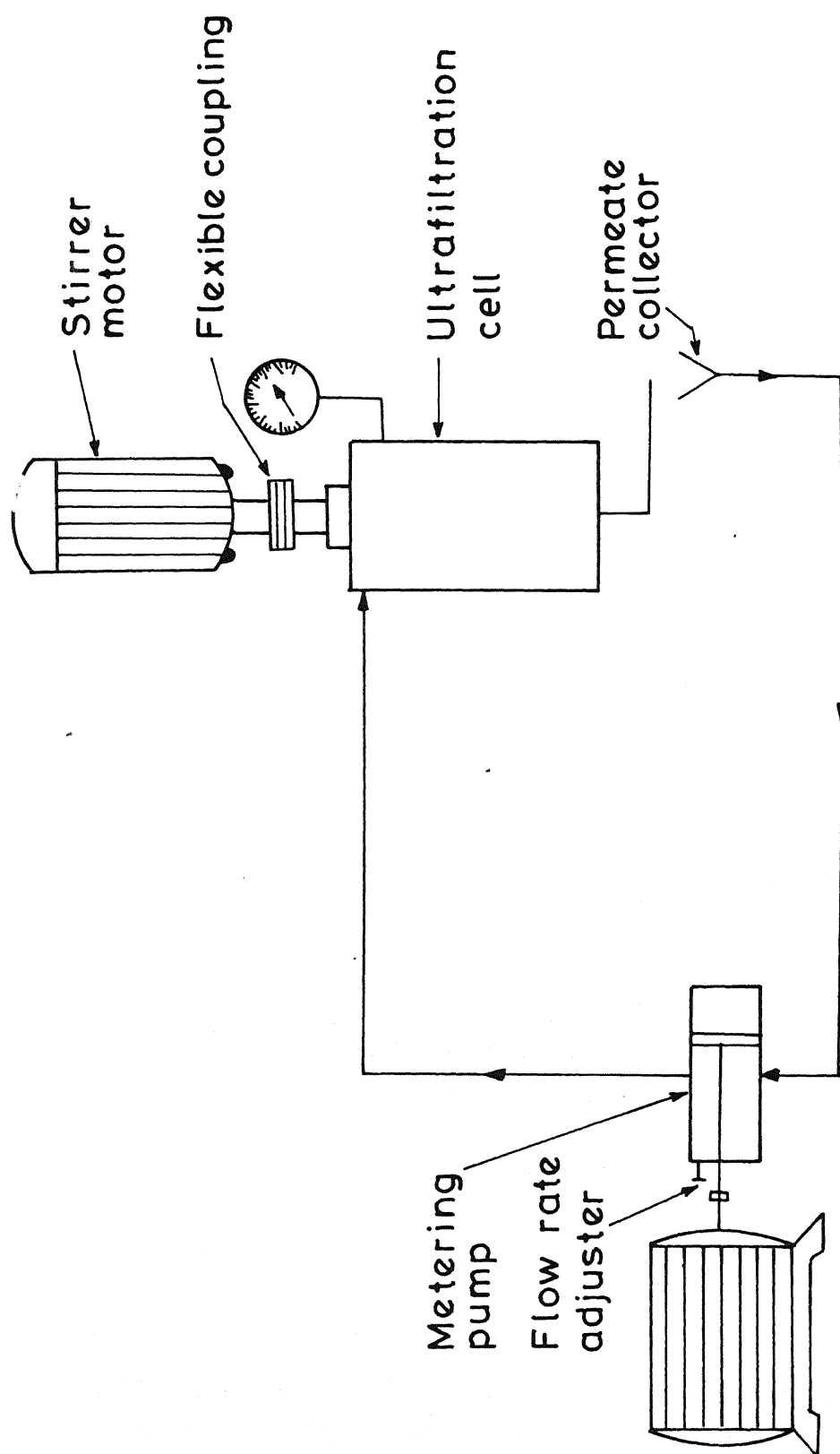
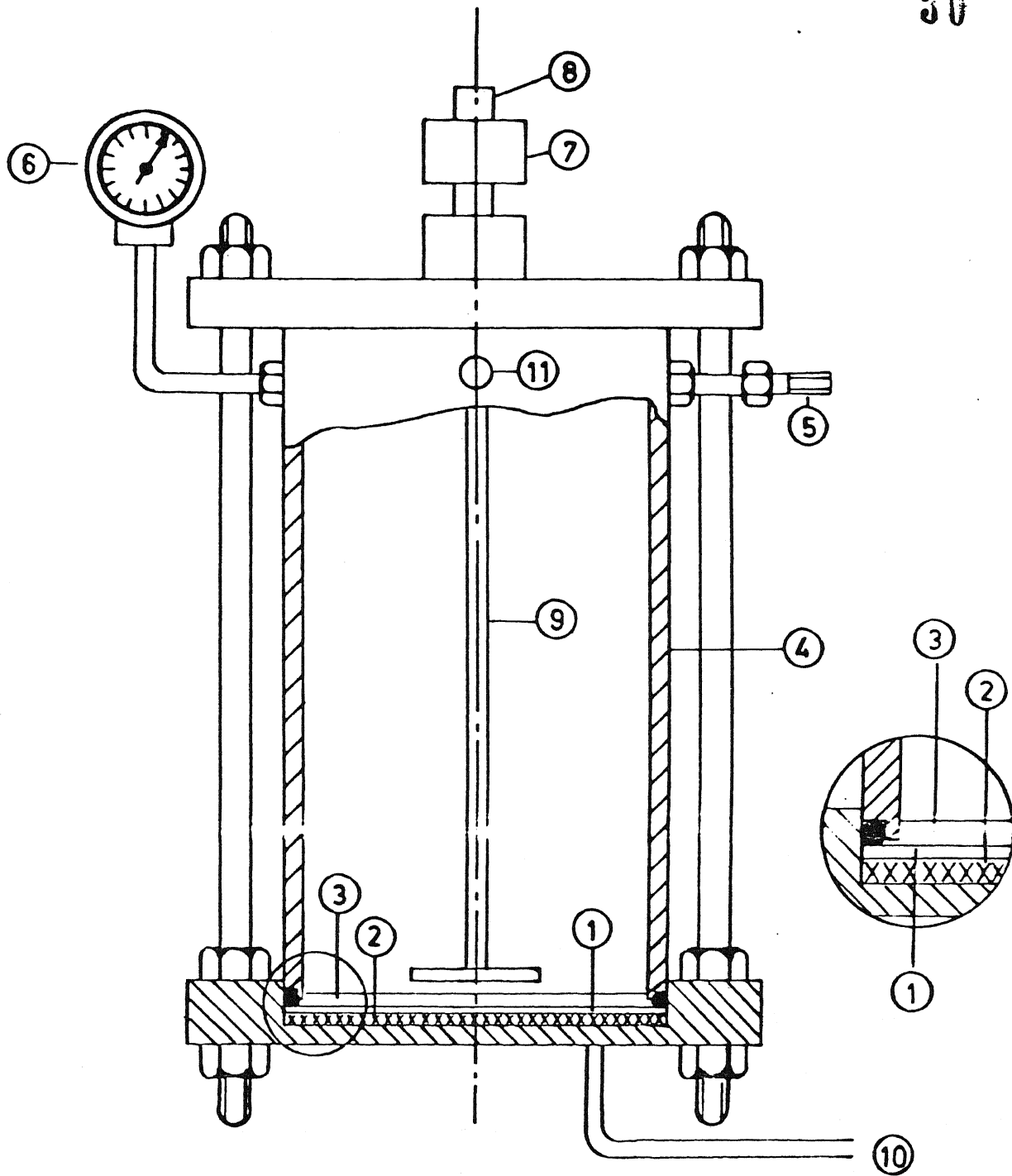


Fig.4.1 Schematic diagram for the experimental setup



1. Membrane, 2. Porous Polyethylene Support, 3. 'O'-Ring  
 4. Cell Body, 5. Pressure Line Connector, 6. Pressure Gauge  
 7. High Pressure Proved Stuffein Box, 8. Adaptor, 9. Stirrer  
 10. Sample Outlet, 11. Feed Sample Inlet.

Fig. 4.2 Ultrafiltration cell.

Material of construction	SS-316
Useful volume	450cc
Residual volume	nil
Membrane diameter	76mm
Effective filtration diameter	26.4 cm <sup>2</sup>
Maximum testing pressure	500 psig
Stirring facility	mechanical

#### 4.2.2 Solutions:

Solutions of Poly Ethylene Glycol(PEG-6000) of molecular weight range 6000-7500 and Black Liquor(BL) were prepared using distilled water. PEG-6000 of A.R. grade was obtained from Fluka, England, while BL (approximately 16% total dissolved solids) was obtained from Central pulp mills, Surat. Solutions of 1% ,2% ,5% concentrations of PEG-6000 and BL were prepared.

#### 4.2.3 Design of experiments:

Experiments were designed so that the effects of three major independent variables, pressure differential, bulk concentration and stirrer speed were studied. The experiments were done so that when two variables (e.g. pressure and concentration) were fixed, the third variable (e.g. stirrer speed) was changed for each experiment until all its levels were exhausted.

The levels for concentration were 1% ,2% and 5% while the pressures were varied as 40psi, 80psi, 100psi and stirrer speeds were varied as 325rpm, 450rpm and 530rpm. The standard levels of the variables were chosen as 80psi, 450rpm and 2% concentration. Of these, two were variables fixed while the third was different for



each experiment.

#### 4.3 Experimental procedure:

After the experimental levels of the variables were fixed, the experiments were conducted for each set of variables. The experimental procedure undertaken was as follows:

The fresh porous membrane was placed on a porous support at the bottom of the cell. The cell was then assembled. First and foremost was to allow the compaction of the membrane by pressurising with distilled water at 120psi for 2 hours. The constancy of water flux beyond this time ensures no further compaction of the membrane. This reading is recorded for the membrane's solvent permeability. Once the cell was assembled with a well cleaned and rinsed membrane, the stirrer speed (for the required rpm) was adjusted by regulating the voltage supply through a variate. The rpm was measured by a stroboscope. The feed solution was pumped into the cell by the metering pump. Once the required pressure was attained the pumping of the feed solution was stopped. The permeate was recycled. The constancy of the pressure was adjusted by regulating the pumping rate of the metering pump. The permeate solution that was coming out through the outlet was collected and the time required for collection of 10cc of permeate was also noted. Flux was then calculated from this reading. Such readings were taken after every 15 minutes of the run until flux value was constant for three consecutive readings. All these collected permeate solutions were either recycled or replaced with freshly prepared solutions of equal concentrations, to the cell. There was a marginal increase of the feed temperature due to pumping of the solution, however for

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practical purposes it was neglected and assumed to be constant (ambient temperature).

After each run the whole cell was rinsed with distilled water thoroughly. The membrane was thoroughly washed and rinsed with distilled water for two hours to remove any deposition. The water flux was again checked at standard conditions and recorded. This procedure was repeated for each set of experimental conditions.

#### 4.3.1 Measurement of concentration:

Refractive index calibration method was used to determine the concentration of PEG.

To find the concentration of black liquor solution, 10cc of the solution was evaporated in an oven at 110°C in a pre-weighed petri-dish. The mass of the remaining solids after evaporation was used to calculate the concentration (total dissolved solids).

#### 4.3.2 Measurement of Viscosity and Density of Solutions:

Viscosities were determined by an Ostwald Viscometer for various PEG and BL concentrations in a constant temperature bath.

A correlation for viscosity and concentration was developed from these data (Appendix A-1).

The densities were measured by using a specific gravity bottle (Appendix A-2).

## CHAPTER-5

### RESULTS AND DISCUSSION

#### 5.1 Selection of Black Liquor Concentration:

The concentration and composition of black liquor (BL) varies ,depending upon type of alkaline pulping, capacity of the industry and type of raw materials used for pulp production, etc. The bigger paper mills produces around 15% BL concentration (t.d.s) from brown stock washers, whereas small scale pulp industries discharge BL at a range from 1 to 8% cocentration. The recovery of BL from bigger paper mills is carried out with conventional technique (Chapter 1) whereas smaller paper mills simply discard. There is an urgency to find an economical and simplified procedure to recover the valuable organic as well as inorganic products from BL with simultaneous disposal of treated effluent to river streams, under specified environmental rules. As highlighted in Chapter 1, UF is one such favourable technology to treat BL.

The selection of BL concentration for experimentation plays an important role while studying flux and rejection behaviour of an asymmetric membrane. The following factors have to be considered before choosing the concentration range for the experiments:

(i) The activity and hence the osmotic pressure of the BL solution increases with an increase in the concentration of BL (Barrow, 1966). This results in a sharp decrease in flux. The flux through the membrane becomes too low for any comparative study at higher concentrations.

(ii) Considering the batch cell with the stirrer designed for experimentation, it was observed proper to handle BL of concentration upto 5% only, as BL viscosity increases beyond this limit of concentration.

(iii) Black liquor is basically composed of macromolecules of various sizes in alkaline solution. At slightly higher concentration, clogging of pores of the membrane takes place and reuse of the membranes becomes more difficult.

For these reasons, use of dilute solutions of BL is always recommended for experimental studies. Hence for this work concentrations of 0.5% to 5% BL were chosen to study the effect of operating variables on limiting flux and rejection.

## 5.2 Selection of PEG Concentration:

In order to make a comparative study with BL an unknown molecular weight it is essential that the concentration of standard solute is also of the same range (0.5 to 5%).

## 5.3 Effect of Operating Variables on Permeate Flux:

Differential pressure, bulk concentration and stirrer speed - were the three variables varied to study the effect of flux as a function of time.

### 5.3.1 Effect of Pressure on Permeate Flux:

Fig.5.1 shows the variation of permeate flux with respect to time for a 2% solution. The nature of the curves coincides with the trend shown in Fig.3.2, as expected. The flux for both PEG and BL drops initially and later attains an almost constant level. The flux at  $2.8 \times 10^5$  and  $6.9 \times 10^5 \text{ N/m}^2$  for PEG is less than that of corresponding BL flux. This suggests that although the bulk solution concentration of both are same (2%), the average molecular weight of, the BL may be less compared to PEG. Considering this explanation of

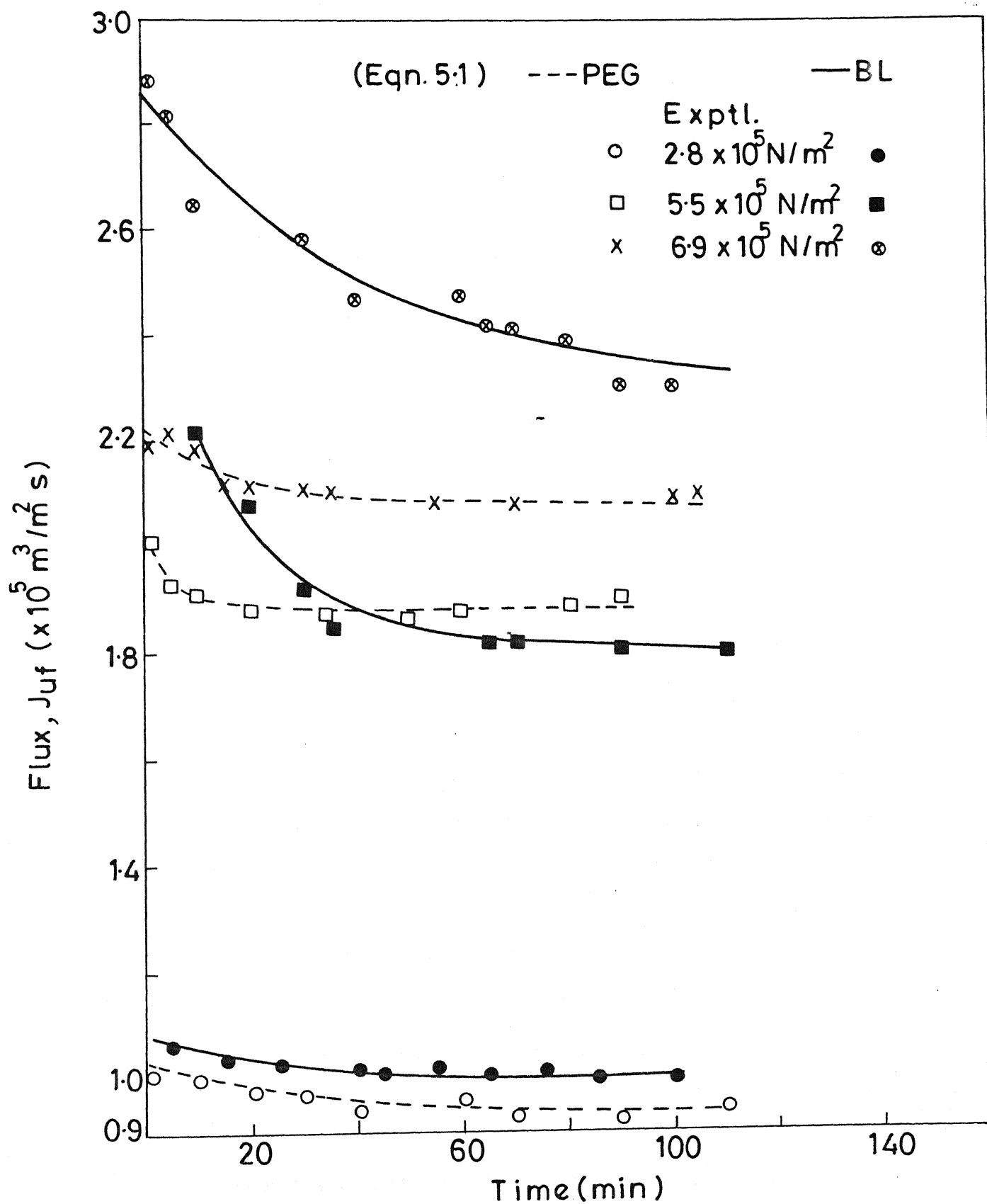


Fig.5.1 Effect of pressure differential on permeate flux  $C_b=2\%$  solution at  $\omega=47.12 \text{ rad/s}$

average molecular weight of BL to be less than that of PEG, the rejection of BL solutes should be much less compared to PEG. It was indeed observed to be so and would be shown later.

On the other hand for the intermediate pressure ( $6.5 \times 10^5 \text{ N/m}^2$ ) the flux of PEG is marginally higher at the later stages inspite of being too low initially than BL. This may be attributed to the fact that BL being a polydispersed solute of wide range of molecular weight, some pores might have been blocked partially. Hence, after some time, one observes lower flux than PEG.

The other fact to note is the time taken to reach the limiting flux increases with increase in pressure for BL. Contrarily this time to reach limiting flux for PEG is nearly same for all the three pressures. This implies that an increase in pressure not only increases the flux but also takes longer time to reach the constant flux for BL. But for PEG it only acts as a catalyst to increase the flux. Further, with the increase in pressure there is a late development of concentrated boundary layer in the case of BL, whereas, PEG solution does not show development of appreciable boundary layer as a function of time. This may be due to the low concentration of PEG. Black liquor, a peculiar polydispersed solution, builds up layer even at low concentration, thus showing different trend at different pressures.

### 5.3.2 Effect of Stirrer Speed on Permeate Flux:

It was obvious from Fig. 5.2 that the permeate flux increases with increase in stirrer speed. It can also be noted that the flux of BL is higher than that of PEG. On the other hand though the initial BL fluxes are higher for 47.12 rad/s and 34.0 rad/s, the limiting flux of BL is less than that of the corresponding PEG curve. This was already discussed in Sec. 5.3.1, due to the

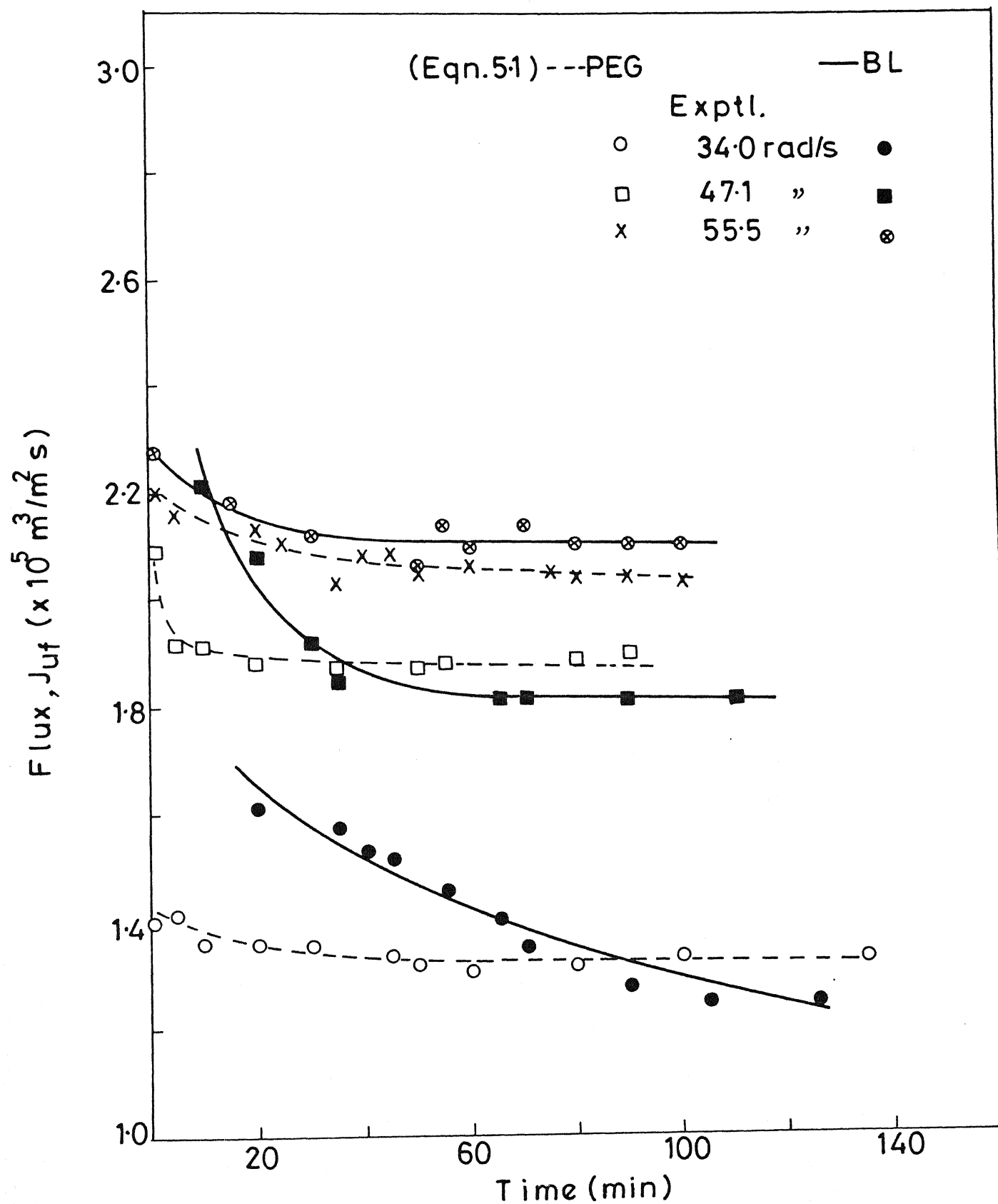


Fig.5.2 Effect of stirrer speed on permeate flux for 2 % solution at  $\Delta P_{\text{app}} = 5.5 \times 10^5 \text{ N/m}^2$

polydispersed nature of BL.

The time for reaching the limiting flux value for BL is distinctly decreasing with an increase in stirrer speed. This may be due to the possibility that the rate of deposition of polarised layer on membrane surface is faster, as Reynolds No. increases. Higher Reynolds No. increases turbulence within the cell which restricts the development of concentrated boundary layer, giving lower diffusive flux than convective flux (Fig.3.3). Higher convective flux, increases the possibility of faster deposition of polarised layer on the membrane surface, because of the polydispersed nature of BL having tendency to precipitate on the surface of the membrane. This gives rise to an earlier break in the curve of Fig.5.2.

It was observed that for PEG solution, this kind of trend is not significant. This seems to be logical considering the nature of PEG solute which does not precipitate. Hence at higher turbulence with more convective flux than diffusive and having much less deposition of polarised layer, the only possibility is to have steady permeate flux.

### 5.3.3 Effect of Concentration on Permeate Flux:

It is a well known fact that as the bulk concentration of the solution increases the permeate flux decreases. This is shown in Fig.5.3. Higher concentrations realises higher osmotic pressure. Hence lower flux is observed. Further, higher concentrations may be giving higher polarised layer resistance which is inversely proportional to flux. However, the trend of curves are identical as bulk concentrations increase at a fixed pressure and stirrer speed. As for PEG solutions, it is apparent (Fig.5.3) that there is not any significant polarisation as a



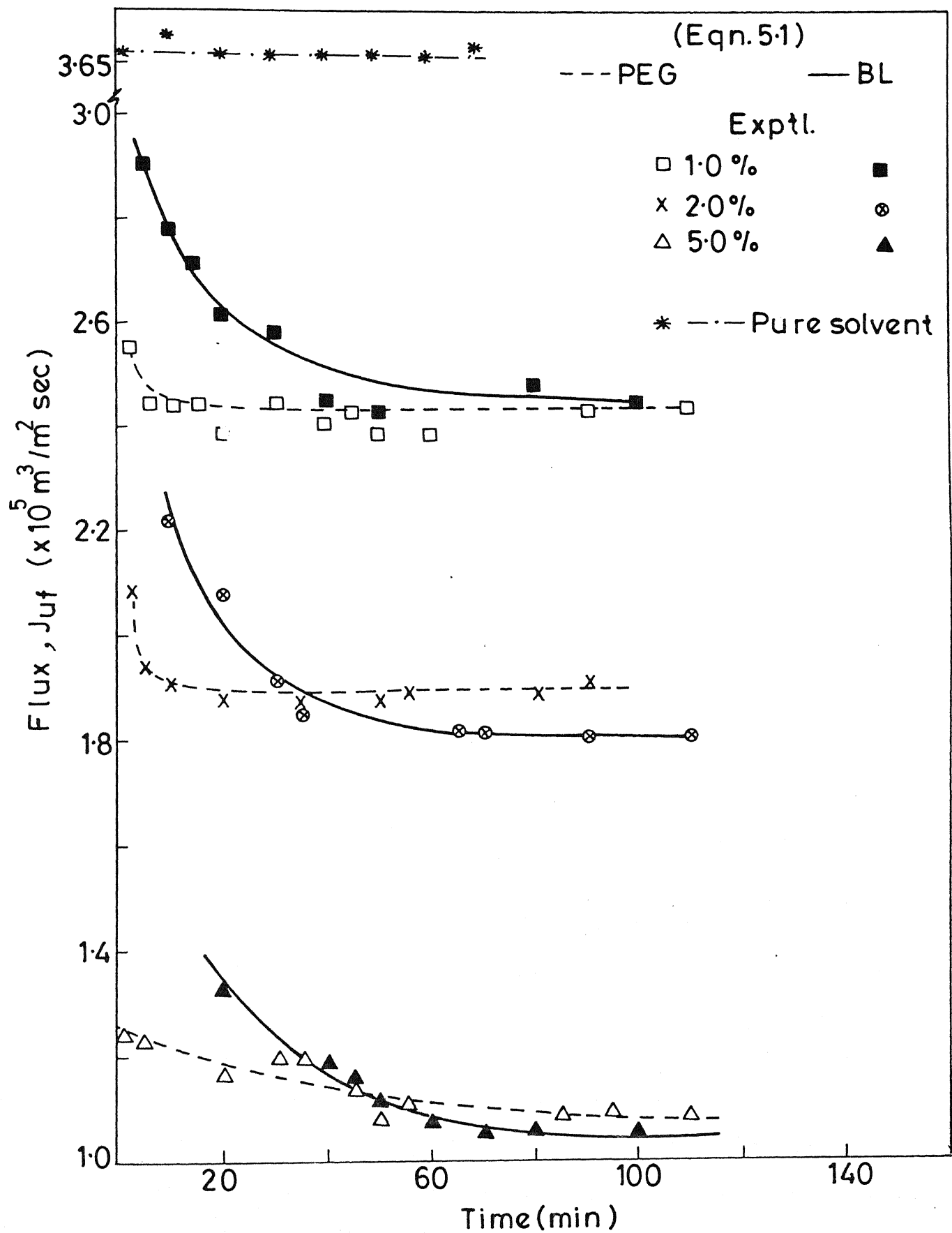


Fig.5.3 Effect of bulk concentration on permeate flux at  $\omega = 47.12 \text{ rad/s}$  and  $\Delta P_{\text{appl}} = 5.5 \times 10^5 \text{ N/m}^2$

function of time, as we increase the bulk concentrations.

#### 5.4 Effect of Operating Variables on Observed Rejection:

The effect of operating variables on observed rejection is shown in Fig.5.4. The permeate concentrations did not vary in a single run for either PEG or BL. Observed rejections were calculated for each run from Eqn.3.20.

##### 5.4.1 Effect of Pressure on Observed Rejection:

The curves obtained for PEG and BL were in contrast. For PEG the observed rejection was independent of pressure at low pressures, while at high pressures it decreases. Goldsmith (1971) and Dasgupta (1986) have tried to explain this. It may be said to be due to the deformation of PEG molecules at pore entrance due to high pressure. This deformation is also aggravated at higher concentrations.

For BL the observed rejection increases with pressure differential initially and at high pressures it forms a plateau. This has also been confirmed earlier (Rajnish, *et al.*, 1985; Poddar, *et al.*, 1989).

Though the actual reason for this relationship is not yet developed, one possible reason could be that BL forms a dynamic membrane (Goldsmith, 1971). Since BL has a wide range of molecular weight, there is a possibility of a dynamic layer being formed by the bigger molecules. The plateau at higher pressure may be explained to be because of the characteristic of the layer formed. This dynamic layer may possibly be a gel layer with essentially constant membrane surface concentration. Hence, initially permeate concentration increases giving lower rejection and later stages shows a plateau.

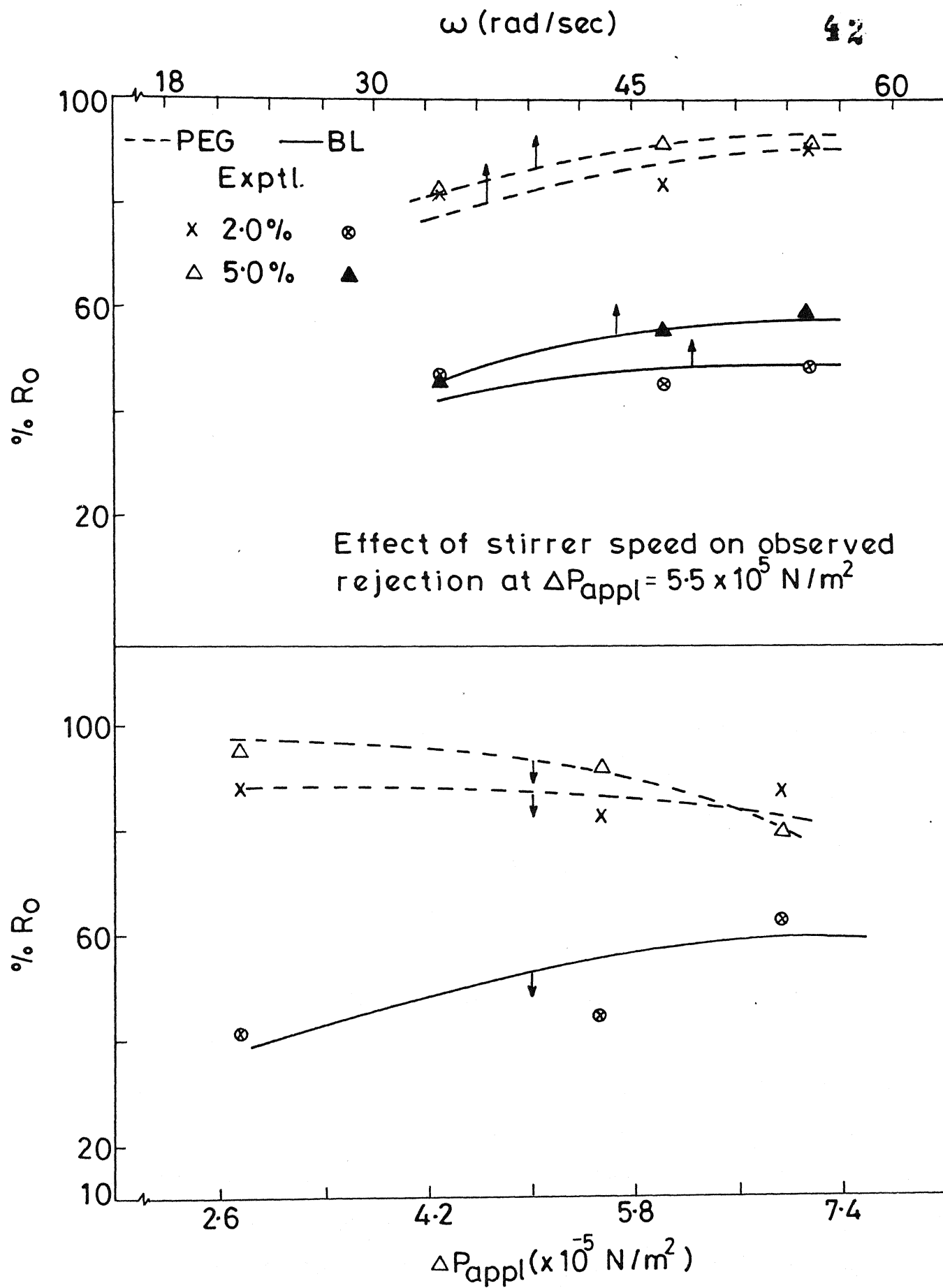


Fig.5.4 Effect of pressure differential on observed rejection at  $\omega = 47.12 \text{ rad/sec}$

#### 5.4.2 Effect of Stirrer Speed on Observed Rejection:

The rejection increases for both PEG and BL with increasing stirrer speeds. However, this rejection attains constancy at high stirrer speeds. This may be explained as follows.

As stirrer speed increases, the feed solution becomes more uniform. This results in a lower membrane surface concentration, hence lower permeate concentration gives increasing rejection. A stage is reached where the solution is totally uniform and no further effect of stirrer speed is noticed on observed rejection.

#### 5.4.3 Effect of Bulk Concentration on Observed Rejection:

As evident from Fig. 5.4 concentration always tends to increase the observed rejection for BL. This may be due to the higher bulk concentration in Eqn. 3.20, and also may be due to a marginal increase in permeate concentrations. Further, higher the bulk concentrations, more are the possibilities of thicker layer deposited on membrane surface giving less amount of permeate solutes; hence <sup>high</sup> ~~less~~ observed rejections.

#### 5.5 Fitting of Experimental Data:

Once the data of flux versus time was obtained, the next step would be to suitably represent the data by an equation with adjustable parameters. The model should be non-linear since the nature of flux versus time curve is highly non-linear. Due to the marked difference of curves (Figs. 5.1 and 5.2) at different set of experimental conditions, this difference has to be taken into account in the model equation.

In favour of the above requirements the following model equation was chosen to fit the data:

$$J_{uf}(t) = \alpha + \beta \gamma^t \quad (5.1)$$

In this equation  $\alpha, \beta$  and  $\gamma$  are adjustable parameters, where  $\gamma$  lies between 0 and 1. The following are the advantages of choosing the model:

(i) At time  $t = 0$ ;  $J_{uf}(0) = \alpha + \beta$  (5.2)

(ii) At time  $t \rightarrow \infty$ ;  $J_{uf}(\infty) = \alpha$  (5.3)

(since  $\gamma$  lies between 0 and 1, the second term on the right of Eqn. 5.1 is negligible with respect to the first term).

(iii) Although simple, the model was versatile and could fit any data within the required range of accuracy.

(iv) Another most important advantage was that by measuring the zero flux,  $J_{uf}(0)$ , the final flux  $J_{uf}(\infty)$  and the UF flux  $J_{uf}(t)$  at any time (say  $t_1$ ) one can calculate  $\gamma$ , from Eqns. 5.1, 5.2 and 5.3. This implies that the whole experiment could be directly modelled by just obtaining the data at three different points, provided the experimental data is accurate enough.

(v) The model also satisfies the inherent nature of UF flux (Figs. 5.1, 5.2 and 5.3) i.e., the drop in flux is, in an UF run, falling with respect to time.

Due to these advantages the model (Eqn. 5.1) was fitted to each and every experiment and the parameters were estimated.

To check the validity of the model, for each run after estimating the parameters, an F-Test was conducted at a confidence level of 0.95. The computer program and the results are presented in appendix.

The predictions of the model for all experiments is shown by a continuous bold line for BL and a continuous broken line for PEG in Figs. 5.1, 5.2 and 5.3. The points shown in the same figures are

real experimental data. There exists an excellent agreement between the experimental data and the model predictions.

## 5.6 Analysis of Experimental Results:

### 5.6.1 Analysis with PEG-6000:

The deviation of the UF flux (Fig.5.3) from the solvent flux may be explained by either osmotic pressure model or gel layer model. The former is more likely for lower molecular weight solutes, while the latter for higher molecular solutes (Doshi, 1985).

PEG-6000 is a lower molecular weight polymer. Also the molecular average weight of BL was found to be around 1500, since it was a degraded BL. So flux limitations through osmotic pressure model is most likely (Eqn.3.5).

For a time dependent case Eqn.3.6 is a possible way to explain flux limitation. In Eqn.3.7,  $J_{uf}(F)$  was obtained from Eqn.5.1 at a constant flux stage with respect to time, which also corresponds to the final fluxes in Figs.5.1, 5.2 and 5.3. Further, it was observed that beyond 110 minutes the final flux,  $J_{uf}(F)$ , for all the experiments attained the limiting flux value; hence this time was taken as the limiting time.  $R_p(F)$  was then calculated from Eqn.3.7. A detailed procedure for calculating  $R_p(F)$  is presented in the appendix (A-4). The results are shown in Tables A-4.1.

### 5.6.2 Analysis with Black Liquor:

$R_p(F)$  for BL was estimated in an identical way as for PEG, except for the difference in calculating mass transfer coefficient  $k$ . Since  $k$  cannot be obtained using Eqn.3.10 as the properties of BL are unknown, velocity variation technique (Sec.5.3) was employed to estimate  $k$ . Equation 3.24 was plotted using experimental data for BL and the slope was obtained from Fig.5.5. The results are shown in Table A-4.2.

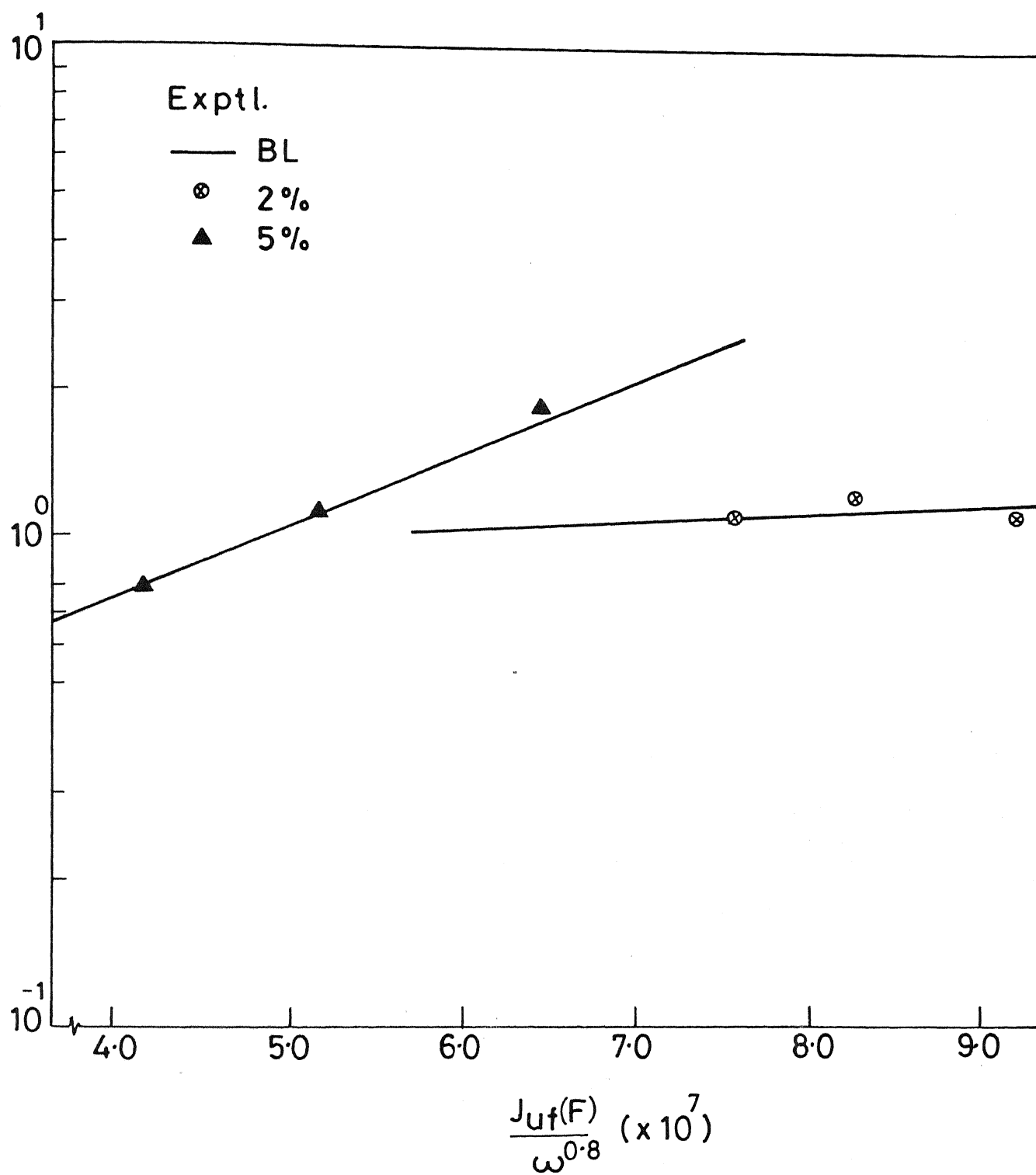


Fig.5-5 Estimation of mass transfer coefficients for BL by velocity variation technique at  $5.5 \times 10^5 \text{ N/m}^2$

### 5.7 Development of Correlation between $R_p(F)$ and the System variables:

In UF systems it becomes necessary to have some idea of how the polarised layer resistance varies with the influencing parameters. In this work an attempt has been made to correlate  $R_p(F)$  with the operating variables.

$R_p$  is a function of membrane surface concentration, flow pattern (characterised by stirrer Reynold's No.), distance between the stirrer and the membrane surface, system geometry (baffles, channels, etc.), Froude No., applied pressure differential, etc.

Since the geometry of the system is fixed for all the experiments, its effect can be neglected. Hence the effective variables are  $\Delta P_{appl}$ ,  $C_m$  and  $N_{Re}$ . The stirrer Reynold's No. is defined by  $D^2 N \rho / \mu$ .

$N_{Re}$ ,  $C_m$  and  $\Delta P_{appl}$  have been employed in the form of dimensionless variables of the order of unity in order to obtain a simplified correlation.  $R_p$  was made dimensionless by dividing by  $R_m + R_a$ . So the final form of the relationship becomes,

$$\frac{R_p(F)}{R_m + R_a} = f \left( \frac{C_m}{\rho_s}, \frac{\Delta P_{appl}}{\Delta \Pi}, N_{Re} \right) \quad (5.4)$$

The experimental values of  $\frac{R_p(F)}{R_m + R_a}$  were plotted

against  $\frac{C_m}{\rho_s}$  and  $N_{Re}$  separately. (Figs. 5.6, 5.7 and 5.8). The



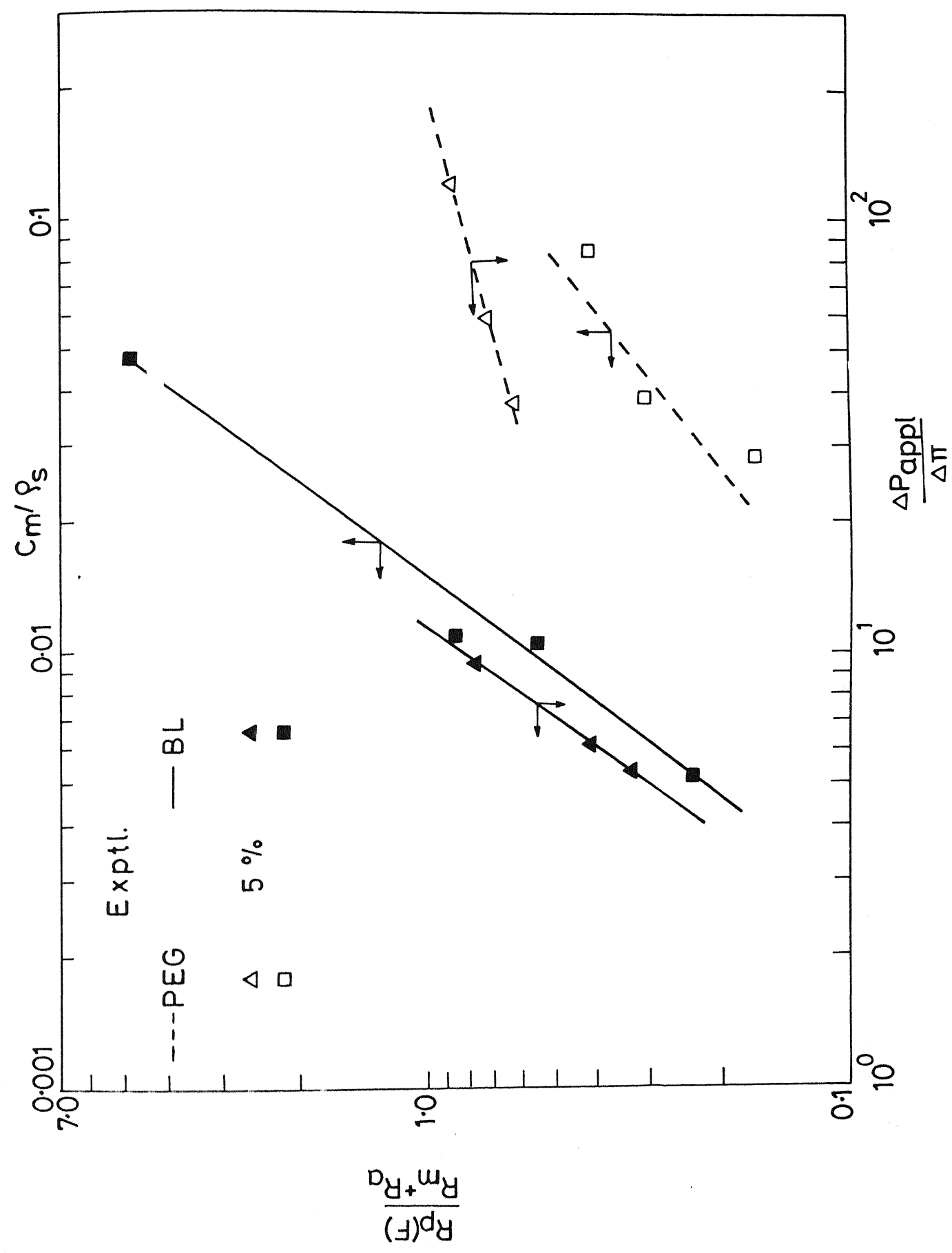


Fig.5.6 Effect of  $\Delta P_{appl}/\Delta \pi$  and  $C_m/\rho_s$  on  $R_p(F)/R_m + R_d$

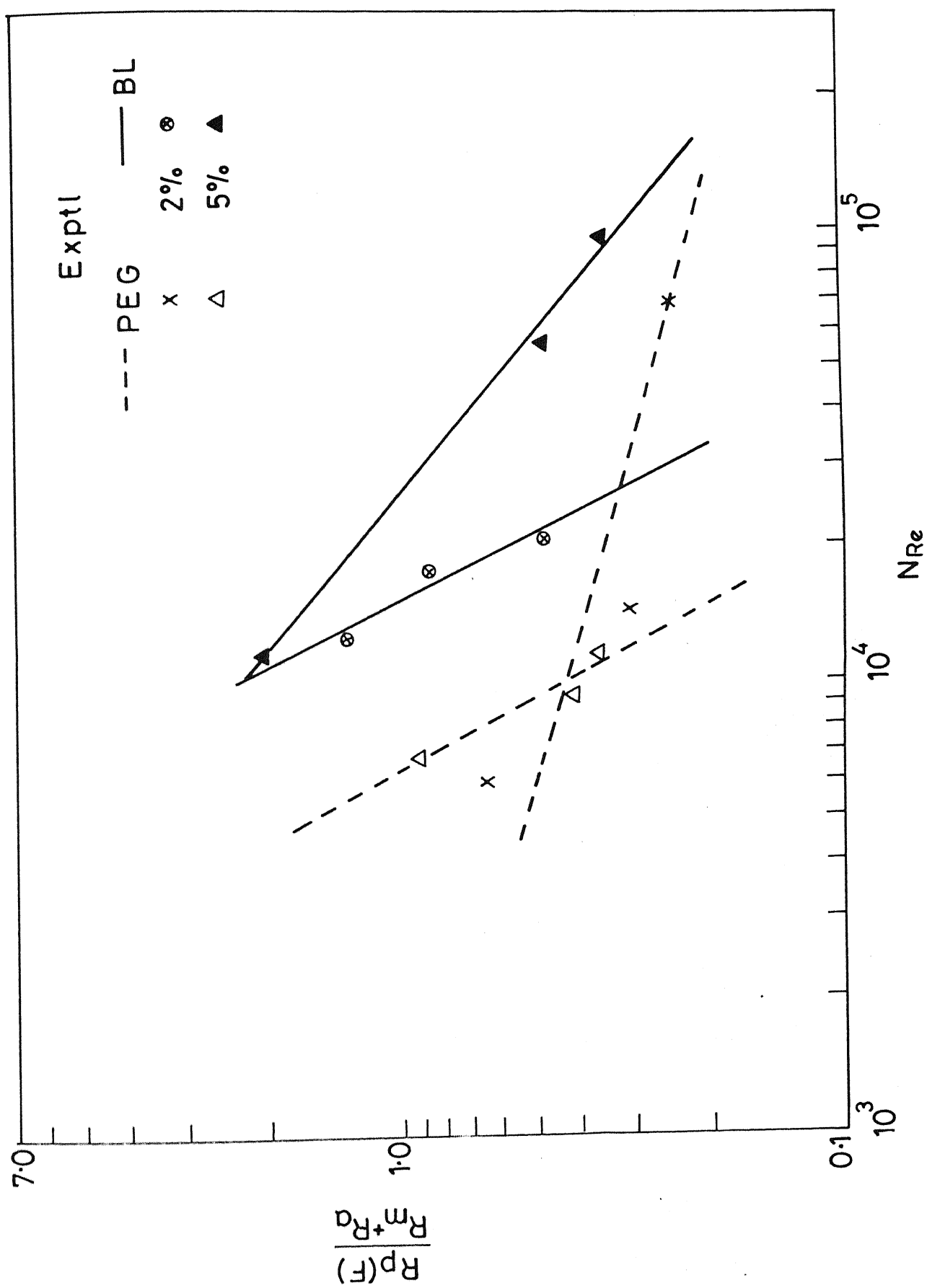


Fig.5.7 Effect of  $N_{Re}$  on  $R_p(F)/R_m + R_a$

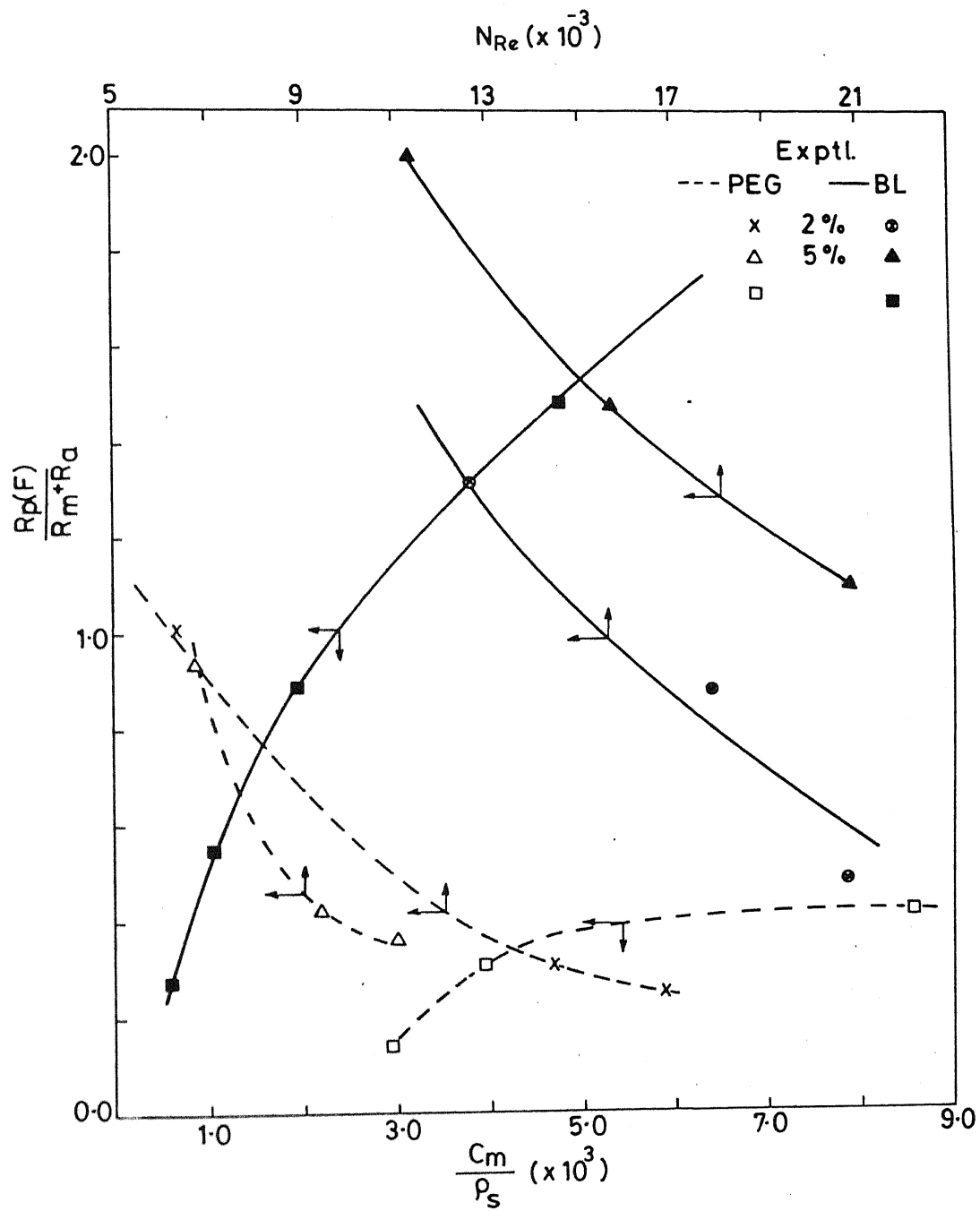


Fig.5.8 Effect of  $C_m/\rho_s$  and  $N_{Re}$  on  $R_p(F)/(R_m+R_a)$

linearity obtained on log-log plots (Figs.5.6 and 5.7) implied a relationship of the form:

$$\frac{R_p(F)}{R_m + R_a} = a \left( \frac{C_m}{\rho_s} \right)^b \left( \frac{\Delta P_{appl}}{\Delta \Pi} \right)^c \left( N_{Re} \right)^d \quad (5.5)$$

The values of a,b,c and d were estimated by least-square curve fit in a log-log form. After solving Eqn 5.5 the results obtained were, as follows:

PEG-6000:

$$\frac{R_p(F)}{R_m + R_a} = 0.95396 \left( 10^{1.2989} \frac{C_m}{\rho_s} \right)^{0.94866} \left( \frac{\Delta P_{appl}}{10 \Delta \Pi} \right)^{-1.0084} \left( 10^4 N_{Re} \right) \quad (5.6)$$

Black Liquor:

$$\frac{R_p(F)}{R_m + R_a} = 3.52933 \left( 10^{0.44693} \frac{C_m}{\rho_s} \right)^{0.04288} \left( \frac{\Delta P_{appl}}{10 \Delta \Pi} \right)^{-1.6887} \left( 10^4 N_{Re} \right) \quad (5.7)$$

The positive values for 'a', 'b' and 'c' and negative value for 'd' clearly indicates that the polarised layer resistance increases with  $C_m/\rho_s$  and  $\Delta P_{appl}/\Delta \Pi$ , while it decreases with  $N_{Re}$ . The experimental and predicted values were plotted and are shown in Fig.5.9. The figure shows a good agreement between the correlation and the results.

The deviations of BL may be due to pore clogging which increases the resistance, while it may also be due to excess passage of lower molecular weights of BL thus decreasing the resistance.

The correlations (Eqns.5.6 and 5.7) may serve as an useful tool for estimating the extent of polarisation as a function of

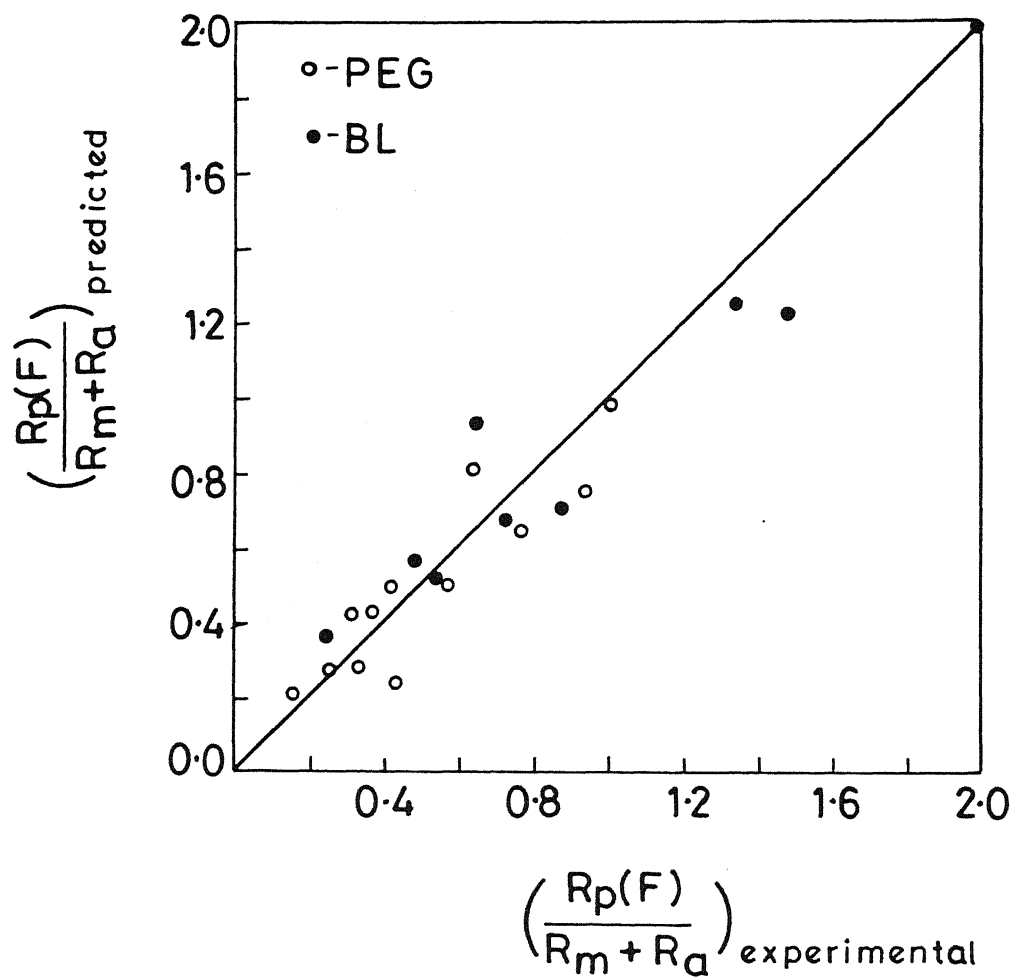


Fig.5-9 Comparison between experimental and predicted values of  $R_p(F)/(R_m+R_a)$

operating variables. Further, this may also predict the limiting flux phenomena to design an UF plant. However, the results obtained are for batch cell operated in a continuous mode. Hence further work is needed to generate experimental data out of tubular or spiral wound modules.

### 5.8 Overall Analysis of Results:

A deep study of the Figs. 5.6, 5.7 and 5.8 coupled together with Figs. 5.1, 5.2, 5.3 and 5.4 has to be done.

The linearly increasing nature of  $R_p(F)/(R_m + R_a)$  with respect to  $C_m/\rho_s$  and  $\Delta P_{\text{appl}}/\Delta \Pi$  and linearly decreasing nature with  $N_{\text{Re}}$  (Figs. 5.6 and 5.7) suggests some conclusions.

An increased drop in rejection (Fig. 5.4) along with increasing  $R_p(F)/(R_m + R_a)$  for PEG at high pressures suggests a boundary layer made of deformed PEG molecules but still resistant to the flow.

For BL a constancy in rejection at high pressures (Fig. 5.4) with a late limitation (Fig. 5.1) and increasing  $R_p(F)$  (Fig. 5.7) suggests continuous formation of polarised layer. This may be elaborated that as the pressure increases convective flux continue to increase which continue to form polarised layer on the membrane surface. This phenomena exhibits continuous fall of flux as the pressure increases.

(iii) Higher stirrer speed forms an early limitation (Fig. 5.2), higher rejection (Fig. 5.4) and lesser  $R_p(F)$  (Figs. 5.7 and 5.8) for BL. This suggests a lower back diffusive flux. So in this case osmotic pressure may not be controlling.

## CHAPTER-6

### CONCLUSIONS AND RECOMMENDATIONS

Ultrafiltration of PEG-6000 and Black liquor solutions using an asymmetric membrane and analysis of the experimental results as was done in this work leads to the following conclusions:

(i) Black liquor has a significant tendency to form a polarised layer while PEG does not have so.

(ii) Continuous formation of polarised layer on membrane surface with increasing pressure results in a continuous fall of permeate flux for BL while insufficient formation of polarised layer for PEG does not exhibit significant fall in permeate flux as a function of time.

(iii) Higher convective flux due to higher Reynold's No., tends to precipitate BL on membrane surface earlier showing limitations in permeate flux compared to lower Reynold's No.

(iv) PEG solutions behaviour may be concluded by the control of osmotic pressure model; while BL is not obeying totally osmotic pressure model. Hence, polarised layer deposition phenomena truly represents the limiting flux characteristics of BL.

The following recommendations are made for future work in this area:

(i) Intermediate values of  $R_p(t)$  should be found in order to detect the exact nature of variation of the polarised layer resistance.

(ii) The mass transfer coefficient has to be determined at the membrane surface concentration. To achieve this an iterative way could be adopted to find the diffusivities. This also needs the physical properties of PEG and BL to be estimated beforehand at such high concentrations.

(iii) The theories of adsorption or interaction of solute to membrane should be investigated to quantify adsorption resistance ( $R_a$ ).



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APPENDIX AA-1 Determination of Viscosity-Concentration Correlation for Black-Liquor and PEG-6000.TABLE A-1.1 Viscosity-Concentration Data for PEG-6000

Solute:PEG-6000

Temperature 30°C

Concentration	Time of Fall	Density	$\mu_s = \frac{C_s t_s}{0.999567 t_w}$
			cP
%	t(sec)	gm/cc	
0 (water)	360.6	0.995678 <sup>*</sup>	0.8500000 <sup>*</sup>
1.0	431.67	0.99809963	1.0200000
2.5	561.40	1.0020412	1.3317794
5.0	801.20	1.0068429	1.9097190
10	1506.4	1.0136519	3.6149594

\* Handbook for Chemical Engineers, Perry, J.H., VI Edn,  
McGraw-Hill, New York.

TABLE A-1.2 Viscosity-Concentration Data for BL

Solute:BL			Temperature:30°C
Concentration %	Time of Fall t(sec)	Density gm/cc	$\mu_s = \frac{C_s t_s}{0.995678 t_w}$ cP
0(water)	360.60000	0.9956780*	0.850000*
0.5	371.76800	0.9977921	0.878188
1.0	381.14480	0.999414	0.902275
2.0	396.46000	1.005848	0.944088
4.495	447.0660	1.020878	1.080488

The following correlations have been obtained for the viscosity-concentration data by polynomial fit of the data(Poddar,T.K.,1986).

$$\mu_{PEG} = 0.85 + 0.1446 C + 0.02734 C^2 - 4.276 \times 10^{-3} C^3 + 2.84 \times 10^{-4} C^4 \quad (A-1)$$

$$\mu_{BL} = 0.85 + 0.06147 C - 1.117 \times 10^{-2} C^2 + 1.98 \times 10^{-3} C^3 \quad (A-2)$$

where C is the concentration of the solution expressed in percent (%) gm of solute in 100cc of solution.

\* Handbook for Chemical Engineers,Perry,R.H,VI Edn,  
McGraw Hill,NewYork.



A-2 Determination of Density of Solution for Black Liquor and PEG-6000:

TABLE A-2 Density-Concentration Data for PEG and BL

Solution	Concentration (%)	Specific Gravity	Density gm/cc
PEG-6000	1.0	1.0024288	0.9980963
	2.5	1.0063908	1.0020412
	5.0	1.0112134	1.0068429
	10.0	1.0180519	1.0136519
BL	0.5	1.0021223	0.9977921
	1.0	1.0042820	0.9999414
	2.0	1.0102143	1.0058482
	4.495	1.0102143	1.022878

A-3 Determination of Concentration of PEG-6000 by Refractometer:

Refractive Index of PEG-6000 at various concentrations were measured at 30°C. The Fig.A-1 shows the calibration curve of Refractive Index versus concentration (gm per 100cc) of PEG-6000. Table A-3 shows the Refractive index-concentration data.

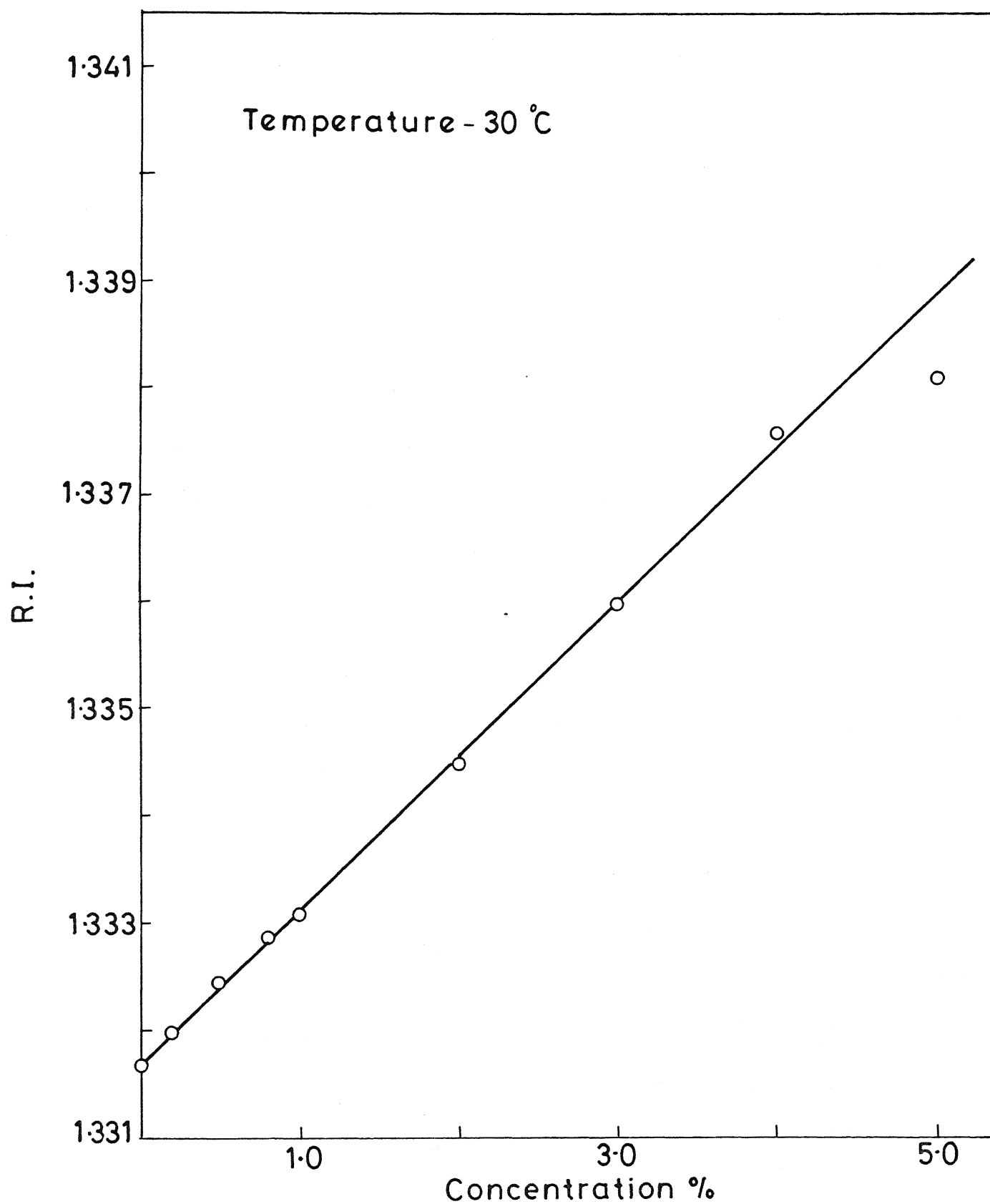


Fig.A-1 Calibration curve for PEG-6000 concentration measurement

**TABLE A-3** RefractiveIndex-Concentration Data for PEG  
Temperature:30°C

Concentration %	R.I.	Concentration	R.I
0.0	1.3317	2.0	1.3345
0.2	1.3320	3.0	1.3360
0.5	1.3325	4.0	1.3376
0.8	1.3329	5.0	1.3381
1.0	1.3331		

**A-4** Calculation of Flux, Observed Rejection and  $R_p(F)$ :

The following steps were carried out in a sequential order to calculate various quantities to estimate  $R_p(F)$ .

(i) The  $R_m$  value was obtained from Eqn.3.1 using the pure solvent flux for the fresh membrane.

(ii) The value for  $R_m + R_a$  of after every experiment was calculated since the pure solvent flux was already obtained from experiment(Eqn.3.3).

(iii)For a paritcular feed concentration ( $C_b$ ),mass transfer coefficient (k) was calculated from Eqns.3.10 and 3.11 for PEG.For Black Liquor the velocity variation technique (Sec.3.5 and Fig.5.5) was employed to calculate the mass transfer coefficient. For these calculations the physical properties were obtained from Tables A-1 and A-2.

(iv) The flux of the ultrafiltration experiments was fitted to model equation (Eqn.5.1).

(v) The final flux  $J_{uf}(F)$  was calculated from Eqn.5.1 at a time  $T(F)$  (110 min) when there was no change in UF flux (Sec.5.6.1).

(vi) The membrane surface concentration ( $C_m$ ) was then calculated from Eqn.3.9 using the final flux  $J_{uf}(F)$  from step v.

(vii) The osmotic pressures for the permeate ( $\pi_p$ ), and for the membrane surface ( $\pi_m$ ) were calculated from Eqns.3.15 through 3.19 using the experimental value of  $C_p$  and the calculated value of  $C_m$ . Subsequently  $\Delta\pi$  ( $\pi_m - \pi_p$ ) was calculated.

(viii)  $R_p(F)$  was then calculated, since all other quantities are known in Eqn 3.7.

(ix) The above steps were repeated for all runs.

TABLE A-4.1

PEG-6000

EXP REFNO	$\Delta P$ $N/m^2$	$C_b$ $kg/m^3$	$\omega$ rad/s	$C_p$ $kg/m^3$	$\mu$ $kg/ms \times 10^3$	$\rho$ $kg/m^3 \times 10^{-3}$	$\nu$ $m^2/s \times 10^6$
00	55163.3	16.667	20.944	1.333	1.1527	0.9985	1.1528
01	55163.3	16.667	47.124	2.750	1.1527	0.9985	1.1528
02	55163.3	9.167	47.124	0.2216	1.0038	0.99809	1.0057
03	55163.3	44.670	47.124	3.5336	1.7823	1.0058	1.7720
04	55163.3	16.667	34.034	3.0000	1.1526	0.9999	1.1528
05	55163.3	16.000	5.502	1.3330	1.1388	0.9967	1.1426
06	689516.6	16.667	47.124	2.000	1.15266	0.9985	1.1528
07	275806.6	16.667	47.124	2.000	1.15266	0.9985	1.1528
08	55163.3	44.67	34.034	7.857	1.7823	1.0058	1.7720
09	55163.3	43.83	55.502	3.803	1.7625	1.0057	1.7526
10	689516.6	41.33	47.124	8.333	1.704	1.0051	1.6951
11	275806.0	44.00	47.124	2.0	1.7665	1.0056	1.7565

...continued

Table A-4.1 (continued)

$k$ $\times 10^5$ m/s	$J_{uf}(F)$ $\times 10^5$ m/s	$C_m$ kg/m <sup>3</sup>	$X$	$\gamma_{1m}$	$\gamma_{2m}$ $\times 10^2$	$\gamma_{1p}$	$\gamma_{2p}$ $\times 10^3$
1.009	1.4742	67.410	331.72	0.940	5.992	0.9988	1.184
1.931	1.8899	39.791	331.72	0.9646	3.537	0.9975	2.44
2.058	2.435	29.364	332.29	0.965	3.499	0.9980	1.967
1.579	1.068	84.413	329.75	0.9249	7.503	0.9968	3.140
1.488	1.326	36.322	331.72	0.9677	3.229	0.9973	2.666
2.210	2.045	38.331	331.72	0.9659	3.401	0.9988	1.184
1.931	2.072	44.899	331.72	0.9600	3.990	0.9982	1.777
1.931	0.935	25.813	331.72	0.9770	2.229	0.9782	1.777
1.217	0.751	76.03	329.29	0.9324	6.758	0.993	6.894
1.810	1.116	77.908	329.8	0.9307	6.925	0.9966	3.380
1.615	1.169	76.362	329.95	0.9321	6.787	0.9925	7.407
1.586	5.569	61.665	329.79	0.9451	5.481	0.9982	1.777

...continued

Table A-4.1 (continued)

$\pi_m$ $N/m^2$	$\pi_p$ $N/m^2$	$\Delta\pi$ $N/m^2$	$J_s^* \times 10^5$ $m/s$	$R_m + R_a \times 10^{-13}$ $Ns^2/m^2 kg$	$R_p(F) \times 10^{-13}$ $Ns^2/m^2 kg$
60758.5	510.49	60248.1	3.5178	1.8447	1.1321
25741.6	1152.18	24589.4	3.5415	1.8324	0.5744
25373.6	86.018	25287.6	3.7835	1.7152	0.3246
91818.8	1400.7	90418.1	3.7502	1.7304	0.7072
22427.1	1225.6	21201.5	3.6427	1.7814	1.7393
32124.4	1898.2	30225.8	3.6726	1.7670	0.4571
30895.1	810.3	30084.7	3.7622	1.7249	0.9941
13882.4	810.3	13072.1	3.5234	1.8418	0.7116
75491.2	3308.8	72182.3	3.7039	1.7520	1.7426
78911.1	1517.0	77394.0	3.7304	1.7396	0.6583
76038.1	3539.6	72498.5	3.7529	1.7292	1.3583
52051.8	786.8	51264.9	3.8159	1.700	0.5814

...continued

Table A-4.1 (continued)

$\frac{R_p (F)}{R_m + R_a}$	$\frac{C_m}{\rho_s}$	$\frac{\Delta P_{appl}}{\Delta \Pi}$	$N_{Re}$
0.643433	.006742	9.15569	6387.11
0.31141	0.03979	22.4329	14371.0
0.17718	0.02936	21.8135	16500.51
0.41232	0.08392	6.10069	9349.42
1.0051	0.03632	26.0176	6387.05
0.25658	0.03834	18.2497	16965.9
0.56253	0.0449	22.9196	14371.0
0.041257	0.02581	21.09887	14371.0
0.94615	0.07559	7.6419	6752.36
0.37572	0.07747	7.12733	11028.4
0.7808	0.07596	9.5107	9773.63
0.33624	0.06131	5.38002	9431.86



TABLE A-4.2BLACK LIQUOR

EXP REFNO	$\Delta P$ $N/m^2$	$C_b$ $kg/m^3$	$\omega$ $rad/s$	$C_p$ $kg/m^3$	$\mu$ $kg/ms$ $\times 10^3$	$\rho$ $kg/m^3$ $\times 10^{-3}$	$\nu$ $m^2/s$ $10^6$
20	55163.3	4.083	47.12	2.845	0.8733	0.9977	0.8753
21	55163.3	8.194	47.12	4.363	0.8939	0.9991	0.8947
22	275806.6	17.249	47.12	9.947	0.9329	1.004	0.9290
23	55163.3	16.317	47.12	8.888	0.9291	1.003	0.9257
24	689516.6	27.093	47.12	9.982	0.9739	1.010	0.9641
25	55163.3	17.228	34.03	9.1012	0.932	1.004	0.9289
26	55163.3	18.082	55.50	9.327	0.9364	1.004	0.9319
27	55163.3	44.806	47.12	25.016	1.0792	1.0207	1.0572
28	55163.3	43.393	34.03	23.32	1.0681	1.0199	1.0473

...continued

Table A-4.2 (continued)

$J_{uf}(F)$ $\times 10^5$ m/s	$R_0$ %	$k$ $\times 10^5$ m/s	$C_m$ kg/m <sup>3</sup>	$X$	$\gamma_{1m}$	$\gamma_{2m}$ $\times 10^2$	$\gamma_{1p}$	$\gamma_{2p}$ $\times 10^3$
2.988	30.2	4.768	5.161	392.7	0.995	0.4588	0.9974	2.528
2.45	46.57	4.768	10.76	392.2	0.990	0.957	0.9961	3.878
1.015	42.39	4.768	19.25	390.27	0.983	1.711	0.991	8.841
1.809	45.52	4.768	19.74	390.48	0.982	1.756	0.992	7.900
2.334	63.15	4.768	37.90	387.99	0.966	3.369	0.991	8.873
1.281	47.17	3.675	20.61	390.27	0.981	1.832	0.991	8.09
2.107	48.41	5.43	22.94	390.08	0.979	2.039	0.992	8.291
1.041	55.83	0.644	49.63	383.94	0.955	4.412	0.9778	22.23
0.871	46.26	0.497	47.41	384.25	0.957	4.214	0.979	20.73

...continued

Table A-4.2 (continued)

$n_m$ $N/m^2$	$n_p$ $N/m^2$	$\Delta\Pi$ $N/m^2$	$J_s^* \times 10^5$ $m/s$	$R_m + R_a \times 10^{-13}$ $Ns^2/m^2 kg$	$R_p(F) \times 10^{-13}$ $Ns^2/m^2 kg$
1781.93	944.64	837.283	4.0285	1.6108	0.41383
4076.64	1495.45	2581.19	3.9097	1.6598	0.8957
8395.41	3735.67	4659.75	3.7829	1.7154	1.2017
8657.82	3280.75	5387.06	3.6173	1.794	1.53418
21830.8	3779.58	18051.3	3.3149	1.9576	1.1589
9182.09	3160.55	6021.54	3.509	1.8493	2.6059
10593.2	3479.09	7114.14	3.429	1.8925	0.9098
33698.2	12041.5	21656.7	3.362	1.893	2.8198
31246.1	10937.9	20308.2	3.3672	1.9272	3.8173

...continued

Table A-4.2 (continued)

$\frac{R_p (F)}{R_m + R_a}$	$\frac{C_m}{\rho_s}$	$\frac{\Delta P_{appl}}{\Delta \Pi}$	$N_{Re}$
0.2439	0.00516	658.81	18927.68
0.5560	0.01077	213.70	18517.27
0.7239	0.01917	59.189	17833.05
0.8943	0.01967	102.39	17895.96
0.6459	0.03752	38.197	17183.21
1.3311	0.0205	114.51	12880.44
0.4919	0.02284	91.606	20741.33
1.4899	0.04863	25.470	15669.67
2.0165	0.04648	27.162	11424.94

[illegible]

# RESULTS OF REGRESSION FOR EXP00

ALPHA= .14740824E-04  
 BETA= .16266497E-05  
 GAMMA= .92904900E+00  
 AVG OF DEP VAR Y= .15137460E-04  
 ERR SUM SQUARES= .46496917E-12  
 AVG OF GAMMA POWER X= .24383720E+00

INDEP VARIABLE TIME	DEPEND VARIABLE EXPTL FLUX	GAMA POWER X	YPRED
.10000000E+01	.16464600E-04	.92904908E+00	.16252055E-04
.50000000E+01	.15519000E-04	.69213894E+00	.15866887E-04
.10000000E+02	.15456500E-04	.47905631E+00	.15520077E-04
.20000000E+02	.15481800E-04	.22942495E+00	.15114130E-04
.40000000E+02	.14509000E-04	.52667932E-01	.14826496E-04
.45000000E+02	.14932400E-04	.36453526E-01	.14800121E-04
.60000000E+02	.14792400E-04	.12087024E-01	.14760485E-04
.70000000E+02	.14908900E-04	.57903653E-02	.14750243E-04
.90000000E+02	.14656000E-04	.13289596E-02	.14742986E-04
.11000000E+03	.14655000E-04	.30496656E-03	.14741320E-04

## SAMPLE VARIANCE-COVARIANCE MATRIX

.15449182E-13  
 .78470494E-14  
 .76484167E-13  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00

\*\*\*\*\* ANOVA AND F-EXP00 \*\*\*\*\*  
 SS= .46496917E-12 MEAN SQ= .58121146E-13  
 SS= .27361140E-11 MEAN SQ= .27361140E-11 F SAMPLE= 47.07605  
 NRD ERROR ESTIMATE= .25772886E-06  
 \*\*\*\*\*

# RESULTS OF REGRESSION FOR EXP01

ALPHA= .18899078E-04  
 BETA= .29223692E-05  
 GAMMA= .68970243E+00  
 AVG OF DEP VAR Y= .19181856E-04  
 ERR SUM SQUARES= .12966797E-12  
 AVG OF GAMMA POWER X= .96746751E-01

INDEP VARIABLE TIME	DEPEND VARIABLE EXPTL FLUX	GAMA POWER X	YPRED
.10000000E+01	.20921800E-04	.68970243E+00	.20914987E-04
.50000000E+01	.19301000E-04	.15606617E+00	.19355238E-04
.10000000E+02	.19125000E-04	.24356649E-01	.19702699E-04
.20000000E+02	.18896500E-04	.59324632E-03	.18900811E-04
.35000000E+02	.18746200E-04	.22550769E-05	.18899084E-04
.50000000E+02	.18746200E-04	.85721081E-08	.18899078E-04
.55000000E+02	.18840200E-04	.13378161E-08	.18899078E-04
.80000000E+02	.18934300E-04	.12386261E-12	.18899078E-04
.90000000E+02	.19125500E-04	.30168780E-14	.18899078E-04

## SAMPLE VARIANCE-COVARIANCE MATRIX

.33826109E-14  
 .73027285E-15  
 .11865073E-12  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00

\*\*\*\*\* ANOVA AND F-EXP01 \*\*\*\*\*  
 FRR SS= .12966797E-12 MEAN SQ= .18523996E-13  
 REG SS= .35573738E-11 MEAN SQ= .35573738E-11 F SAMPLE= 192.04138  
 STANDARD ERROR ESTIMATE= .14700792E-06  
 \*\*\*\*\*

## RESULTS OF REGRESSION FOR EXP02

ALPHA= .24305626E-04  
 BETA= .17352258E-05  
 GAMMA= .76819863E+00  
 AVG OF DEPEND VAR Y= .24460350E-04  
 PR SUM SQUARES= .79449629E-12  
 AVG OF GAMMA POWER Y= .89162881E-01

INDEP VARIABLE	DEPEND VARIABLE	GAMA POWER X	YPRED
TIME	EXPTL FLUX		
.10000000E+01	.25656000E-04	.76819863E+00	.25638678E-04
.60000000E+01	.24526500E-04	.20551389E+00	.24662254E-04
.10000000E+02	.24590000E-04	.71570703E-01	.24429822E-04
.15000000E+02	.24590000E-04	.19147096E-01	.24338852E-04
.20000000E+02	.23967100E-04	.51223655E-02	.24314515E-04
.30000000E+02	.24590000E-04	.36661130E-03	.24306262E-04
.40000000E+02	.24120000E-04	.26238628E-04	.24305672E-04
.45000000E+02	.24431000E-04	.70195418E-05	.24305638E-04
.50000000E+02	.23906500E-04	.18779171E-05	.24305629E-04
.60000000E+02	.23967100E-04	.13440384E-06	.24305626E-04
.10000000E+03	.24590000E-04	.35265725E-11	.24305626E-04
.10500000E+03	.24590000E-04	.94345340E-12	.24305626E-04

## SAMPLE VARIANCE-COVARIANCE MATRIX

10494472E-13  
 10467018E-14  
 26043043E-12  
 00000000E+00  
 00000000E+00  
 00000000E+00  
 00000000E+00  
 00000000E+00

\*\*\*\*\* ANOVA AND F-EXP02 \*\*\*\*\*

SS= .70449629E-12 MEAN SQ= .79449629E-13

SS= .16335444E-11 MEAN SQ= .16335444E-11 F SAMPLE= 20.56076

WARD ERROR ESTIMATE= .29711507E-06

\*\*\*\*\*

## RESULTS OF REGRESSION FOR EXP03

ALPHA= .10160911E-04  
 BETA= .23469613E-05  
 GAMMA= .98505720E+00  
 AVG OF DEPEND VAR Y= .11441836E-04  
 PR SUM SQUARES= .85327195E-12  
 AVG OF GAMMA POWER Y= .54578034E+00

INDEP VARIABLE	DEPEND VARIABLE	GAMA POWER X	YPRED
TIME	EXPTL FLUX		
.10000000E+01	.12344000E-04	.98505720E+00	.12472802E-04
.50000000E+01	.12383400E-04	.92748573E+00	.12337684E-04
.20000000E+02	.11687800E-04	.73999528E+00	.11897651E-04
.30000000E+02	.12098000E-04	.63656598E+00	.11654907E-04
.35000000E+02	.12065000E-04	.59040585E+00	.11546571E-04
.45000000E+02	.11257000E-04	.50788470E+00	.11352897E-04
.50000000E+02	.10757000E-04	.47105581E+00	.11266461E-04
.55000000E+02	.11007000E-04	.43689754E+00	.11196293E-04
.85000000E+02	.10757000E-04	.27811411E+00	.10813634E-04
.95000000E+02	.10752000E-04	.23924204E+00	.10722403E-04
.11000000E+03	.10752000E-04	.19087946E+00	.10698898E-04

## SAMPLE VARIANCE-COVARIANCE MATRIX

74017259E-12  
 63897372E-12  
 80350145E-12  
 00000000E+00  
 00000000E+00  
 00000000E+00  
 00000000E+00  
 00000000E+00

\*\*\*\*\* ANOVA AND F-EXP03 \*\*\*\*\*

FRR SS= .85327195E-12 MEAN SQ= .94807995E-13

REG-SS= .38395483E-11 MEAN SQ= .38395483E-11 F SAMPLE= 40.49815

STANDARD ERROR ESTIMATE= .32658689E-06

\*\*\*\*\*

# RESULTS OF REGRESSION FOR EXP05

ALPHA= .20422815E-04  
 BETA= .16982008E-05  
 GAMMA= .95965218E+00  
 AVG OF DEP VAR Y= .20878831E-04  
 FPR SUM SQUARES= .42567446E-12  
 AVG OF GAMMA POWER X= .26852892E+00

INDEP VARIABLE	DEPEND VARIABLE	GAMA POWER X	YPRED
TIME	EXPTL FLUX	.95965218E+00	.22052497E-04
.10000000E+01	.22145300E-04	.81389665E+00	.21804975E-04
.50000000E+01	.21639200E-04	.43881053E+00	.21168003E-04
.20000000E+02	.21394600E-04	.35714642E+00	.21029321E-04
.25000000E+02	.21038100E-04	.23658370E+00	.20824581E-04
.35000000E+02	.20359000E-04	.19255468E+00	.20749811E-04
.40000000E+02	.20806000E-04	.15671961E+00	.20688956E-04
.45000000E+02	.20991000E-04	.12755356E+00	.20639426E-04
.50000000E+02	.20536000E-04	.84495020E-01	.20566104E-04
.60000000E+02	.20670600E-04	.45555297E-01	.20500177E-04
.75000000E+02	.20536000E-04	.37077304E-01	.20485779E-04
.80000000E+02	.20469000E-04	.24561035E-01	.20464524E-04
.90000000E+02	.20450000E-04	.16269911E-01	.20450444E-04
.10000000E+03	.20390000E-04		

## SAMPLE VARIANCE-COVAPAINCE MATRIX

.18763412E-13  
 .11781507E-13  
 .38476581E-13  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00

\*\*\*\*\* ANOVA AND F-EXP05 \*\*\*\*\*

FRR SS= .42567446E-12 MEAN SQ= .38697679E-13  
 REG SS= .32051644E-11 MEAN SQ= .32051644E-11 F SAMPLE= 82.82575  
 STANDARD ERROR ESTIMATE= .20631880E-06

\*\*\*\*\*

# RESULTS OF REGRESSION FOR EXP04

ALPHA= .12254848E-04  
 BETA= .10330439E-05  
 GAMMA= .95152156E+00  
 AVG OF DEP VAR Y= .13555664E-04  
 FPR SUM SQUARES= .17884591E-12  
 AVG OF GAMMA POWER X= .29119354E+00

INDEP VARIABLE	DEPEND VARIABLE	GAMA POWER X	YPRED
TIME	EXPTL FLUX	.95152156E+00	.14237811E-04
.10000000E+01	.14182900E-04	.77999742E+00	.14060619E-04
.50000000E+01	.14236300E-04	.60839596E+00	.13883348E-04
.10000000E+02	.13670900E-04	.37014565E+00	.13637225E-04
.20000000E+02	.13720500E-04	.22519512E+00	.13487484E-04
.30000000E+02	.13602200E-04	.10686573E+00	.13365245E-04
.45000000E+02	.13428500E-04	.83354996E-01	.13340957E-04
.50000000E+02	.13240700E-04	.50712842E-01	.13307236E-04
.60000000E+02	.13103300E-04	.18771139E-01	.13274239E-04
.80000000E+02	.13212000E-04	.69480553E-02	.13262028E-04
.10000000E+03	.13381000E-04	.12204371E-02	.13256109E-04
.13500000E+03	.13334000E-04		

## SAMPLE VARIANCE-COVAPAINCE MATRIX

.73723701E-14  
 .41584739E-14  
 .19336777E-13  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00

\*\*\*\*\* ANOVA AND F-EXP04 \*\*\*\*\*

R SS= .17884591E-12 MEAN SQ= .19871767E-13  
 G SS= .12382138E-11 MEAN SQ= .12382138E-11 F SAMPLE= 62.31020  
 STANDARD ERROR ESTIMATE= .14951836E-06

\*\*\*\*\*



# RESULTS OF REGRESSION FOR EXP06

ALPHA= .20709785E-04  
 BETA= .15923036E-05  
 GAMMA= .95181721E+00  
 AVG OF DEPENDABLE= .21207642E-04  
 AVG OF DEPENDABLE= .80246180E-12  
 FPR SUM SQUARES= .31329253E+00  
 AVG OF GAMMA POWER X= .31329253E+00

INDEP VARIABLE	DEPEND VARIABLE	GAMMA POWER X	YPRED
TIME	EXPTL FLUX		
.10000000E+01	.21965500E-04	.95181721E+00	.22224367E-04
.50000000E+01	.22275600E-04	.78120992E+00	.21952708E-04
.10000000E+02	.21838800E-04	.61028895E+00	.21680550E-04
.15000000E+02	.21274400E-04	.47676378E+00	.21467938E-04
.20000000E+02	.21203000E-04	.37245259E+00	.21301842E-04
.30000000E+02	.21274400E-04	.22730370E+00	.21070721E-04
.35000000E+02	.21038100E-04	.17757191E+00	.20991533E-04
.55000000E+02	.20806000E-04	.66137117E-01	.20814095E-04
.60000000E+02	.20142800E-04	.51666972E-01	.20791054E-04
.70000000E+02	.20875700E-04	.31531782E-01	.20758993E-04
.10000000E+03	.20991400E-04	.71672908E-02	.20720197E-04
.10500000E+03	.20806000E-04	.55991586E-02	.20717700E-04

## SAMPLE VARIANCE-COVARIANCE MATRIX

31007928E-13  
 .17354142E-13  
 .78015841E-13  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00

\*\*\*\*\* ANOVA AND F-EXP06 \*\*\*\*\*

R SS= .80246180E-12 MEAN SQ= .80246180E-13  
 G SS= .29619281E-11 MEAN SQ= .29619281E-11 F SAMPLE= 36.91052  
 STANDARD ERROR ESTIMATE= .29860077E-06

# RESULTS OF REGRESSION FOR EXP07

ALPHA= .93117629E-05  
 BETA= .10759246E-05  
 GAMMA= .96834286E+00  
 AVG OF DEPENDABLE= .96955778E-05  
 AVG OF DEPENDABLE= .20130733E-12  
 FPR SUM SQUARES= .35673019E+00  
 AVG OF GAMMA POWER X= .35673019E+00

INDEP VARIABLE	DEPEND VARIABLE	GAMMA POWER X	YPRED
TIME	EXPTL FLUX		
.10000000E+01	.10234700E-04	.96834286E+00	.10353627E-04
.10000000E+02	.10346600E-04	.72492244E+00	.10091725E-04
.20000000E+02	.98105101E-05	.52551254E+00	.98771749E-05
.30000000E+02	.97098000E-05	.38095583E+00	.97216428E-05
.40000000E+02	.94200400E-05	.27616343E+00	.96088939E-05
.60000000E+02	.97098000E-05	.14512734E+00	.94679090E-05
.70000000E+02	.93272000E-05	.10520607E+00	.94249567E-05
.90000000E+02	.92815100E-05	.55287108E-01	.93712476E-05
.11000000E+03	.94200400E-05	.29054068E-01	.93430230E-05

## SAMPLE VARIANCE-COVARIANCE MATRIX

30028583E-13  
 .19724835E-13  
 .40926035E-13  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00

\*\*\*\*\* ANOVA AND F-EXP07 \*\*\*\*\*

ERR SS= .20140733E-12 MEAN SQ= .28772476E-13  
 REG SS= .98568590E-12 MEAN SQ= .98568590E-12 F SAMPLE= 34.25795  
 STANDARD ERROR ESTIMATE= .18321541E-06

\*\*\*\*\*

# RESULTS OF REGRESSION FOR EXP08

ALPHA= 75002530E-05  
 BETA= .62281030E-06  
 GAMMA= .95108407E+00  
 AVG OF DEP VAR Y= 76578878E-05  
 ERR SUM SQUARES= .63745899E-13  
 AVG OF GAMMA POWER Y= .25310206E+00

INDEP VARIABLE	DEPEND VARIABLE	GAMA POWER X	YPRED
TIME	EXPTL FLUX		
.10000000E+01	.81053000E-05	.95108407E+00	.80925985E-05
.10000000E+02	.77918900E-05	.60560444E+00	.78774301E-05
.20000000E+02	.79057600E-05	.36675673E+00	.77286732E-05
.30000000E+02	.75285000E-05	.22210951E+00	.76385852E-05
.50000000E+02	.75737200E-05	.63392775E-01	.75397349E-05
.65000000E+02	.74252100E-05	.38390946E-01	.75241633E-05
.75000000E+02	.75435000E-05	.23249727E-01	.75147332E-05
.10000000E+03	.75335000E-05	.66357572E-02	.75043858E-05
.14500000E+03	.75136100E-05	.69461027E-03	.75006957E-05

## SAMPLE VARIANCE-COVARIANCE MATRIX

.33956506E-14  
 .20358755E-14  
 .12638017E-13  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00

\*\*\*\*\* ANOVA AND F-EXP08 \*\*\*\*\*

R-SS= .63745899E-13 MEAN SQ= .91065570E-14  
 F-SS= .34316632E-12 MEAN SQ= .34316632E-12 F SAMPLE= 37.68343

STANDARD ERROR ESTIMATE= .10307433E-06

\*\*\*\*\*

# RESULTS OF REGRESSION FOR EXP09

ALPHA= 10917596E-04  
 BETA= .26290186E-05  
 GAMMA= .95263821E+00  
 AVG OF DEP VAR Y= .11798808E-04  
 ERR SUM SQUARES= .81271003E-12  
 AVG OF GAMMA POWER X= .33053770E+00

INDEP VARIABLE	DEPEND VARIABLE	GAMA POWER X	YPRED
TIME	EXPTL FLUX		
.70000000E+01	.12968600E-04	.84593841E+00	.13175422E-04
.15000000E+02	.12622800E-04	.69871057E+00	.12782468E-04
.25000000E+02	.12707500E-04	.55016824E+00	.12386006E-04
.30000000E+02	.12622800E-04	.48819645E+00	.12220602E-04
.35000000E+02	.12375300E-04	.43320526E+00	.12073829E-04
.55000000E+02	.11337900E-04	.26859018E+00	.11634460E-04
.60000000E+02	.11270400E-04	.23833578E+00	.11553719E-04
.65000000E+02	.11137800E-04	.21148927E+00	.11482065E-04
.75000000E+02	.11337900E-04	.16527773E+00	.11362067E-04
.80000000E+02	.11137800E-04	.14776979E+00	.11311997E-04
.90000000E+02	.11270400E-04	.11635468E+00	.11228149E-04
.10500000E+03	.11337900E-04	.81298244E-01	.11134583E-04
.12500000E+03	.11270400E-04	.50405459E-01	.11052130E-04

## SAMPLE VARIANCE-COVARIANCE MATRIX

.11576976E-12  
 .40809822E-13  
 .11004899E-12  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00

\*\*\*\*\* ANOVA AND F-EXP09 \*\*\*\*\*

ERR SS= .83271003E-12 MEAN SQ= .75700912E-13  
 REG SS= .54004964E-11 MEAN SQ= .54004964E-11 F SAMPLE= 71.33991

STANDARD ERROR ESTIMATE= .28956715E-06

\*\*\*\*\*

## RESULTS OF REGRESSION FOR EXP10

ALPHA= .11665721E-04  
BETA= .66563000E-06  
GAMMA= .95661216E+00  
AVG OF DEP VAR Y= .1898100E-04  
ERR SUM SQUARES= .8453289E-13  
AVG OF GAMMA POWER X= .3476034E+00

```
*****
INDEP VARIABLE      DEPEND VARIABLE      EXPIL FLUX      GAMMA POWER X      YPRED
TIME
.10000000E+01      .12451900E-04      .12098500E-04      .96661216E+00      .12310138E-04
.50000000E+01      .12098500E-04      .12060000E-04      .84384224E+00      .12228417E-04
.10000000E+02      .11938700E-04      .11909300E-04      .71206972E+00      .12140704E-04
.30000000E+02      .11909300E-04      .11908300E-04      .36105016E+00      .11907051E-04
.35000000E+02      .11908300E-04      .11908300E-04      .30466938E+00      .11869521E-04
.45000000E+02      .11687800E-04      .11687800E-04      .21694583E+00      .11811129E-04
.50000000E+02      .11833900E-04      .11833900E-04      .18306806E+00      .11788579E-04
.70000000E+02      .11616100E-04      .11616100E-04      .92823428E-01      .11728508E-04
.85000000E+02      .11687800E-04      .11687800E-04      .55775231E-01      .11703847E-04
.90000000E+02      .11687800E-04      .11687800E-04      .47065496E-01      .11698050E-04
.95000000E+02      .11687800E-04      .11687800E-04      .39715853E-01      .11693157E-04
```

## SAMPLE VARIANCE-COVARIANCE MATRIX

.83193358E-14  
.55965336E-14  
.10143069E-13  
.00000000E+00  
.00000000E+00  
.00000000E+00  
.00000000E+00  
.00000000E+00  
.00000000E+00

\*\*\*\*\* ANOVA AND F-EXP10 \*\*\*\*\*

RR SS= .84532890E-13      MEAN SQ= .93925434E-14  
REG SS= .50671358E-12      MEAN SQ= .50671358E-12      F SAMPLE= 53.94850  
STANDARD ERROR ESTIMATE= .10279402E-06

\*\*\*\*\*

## RESULTS OF REGRESSION FOR EXP11

ALPHA= .55537144E-05  
BETA= .85315451E-06  
GAMMA= .96102710E+00  
AVG OF DEP VAR Y= .57759670E-05  
ERR SUM SQUARES= .58562857E-13  
AVG OF GAMMA POWER X= .26050686E+00

```
*****
INDEP VARIABLE      DEPEND VARIABLE      EXPIL FLUX      GAMMA POWER X      YPRED
TIME
.10000000E+01      .64184000E-05      .60492900E-05      .96102710E+00      .63736190E-05
.10000000E+02      .25000000E+02      .58620000E-05      .67197997E+00      .61270172E-05
.25000000E+02      .35000000E+02      .58081000E-05      .37016113E+00      .58695190E-05
.35000000E+02      .45000000E+02      .56689000E-05      .24874087E+00      .57659288E-05
.45000000E+02      .65000000E+02      .56184800E-05      .16714888E+00      .56963182E-05
.65000000E+02      .75000000E+02      .57903000E-05      .75477258E-01      .56181082E-05
.75000000E+02      .85000000E+02      .55041000E-05      .50719206E-01      .55969857E-05
.10500000E+03      .55360000E-05      .55360000E-05      .34082290E-01      .55827918E-05
.11500000E+03      .55041000E-05      .55041000E-05      .15390099E-01      .55668446E-05
.11500000E+03      .55041000E-05      .55041000E-05      .10341838E-01      .55625376E-05
```

## SAMPLE VARIANCE-COVARIANCE MATRIX

.34421833E-14  
.20593090E-14  
.90042276E-14  
.00000000E+00  
.00000000E+00  
.00000000E+00  
.00000000E+00  
.00000000E+00  
.00000000E+00

\*\*\*\*\* ANOVA AND F-EXP11 \*\*\*\*\*

ERR SS= .58562857E-13      MEAN SQ= .73203571E-14  
REG SS= .67917546E-12      MEAN SQ= .67917546E-12      F SAMPLE= 92.77901  
STANDARD ERROR ESTIMATE= .91466510E-07

\*\*\*\*\*

E SAMPLE= 176.10465

## RESULTS OF REGRESSION FOR EXP22

ALPHA = .10150635E-04  
 BETA = .81354645E-06  
 GAMMA = .95162852E+00  
 AVG OF DEP VAR Y = .10308600E-04  
 PR SUM SQUARES = .5711140E-13  
 VG OF GAMMA POWER X = .19416856E+00

\*\*\*\*\*  
 INDEP VARIABLE DEPEND VARIABLE  
 TIME EXPTL FLUX

TIME	EXPTL FLUX	GAMA POWER X	YPRED
.5000000E+01	.10819600E-04	.78043590E+00	.10785556E-04
.1500000E+02	.10460900E-04	.67534805E+00	.10537353E-04
.2500000E+02	.10403400E-04	.28952508E+00	.10386177E-04
.4000000E+02	.10290300E-04	.13762518E+00	.10262599E-04
.4500000E+02	.10152400E-04	.10740763E+00	.10238016E-04
.5500000E+02	.10346600E-04	.65419861E-01	.10203857E-04
.6500000E+02	.10179700E-04	.39845942E-01	.10183051E-04
.7500000E+02	.10290300E-04	.24269374E-01	.10170379E-04
.8500000E+02	.10071400E-04	.14781995E-01	.10162661E-04
.1000000E+03	.10071400E-04	.70265925E-02	.10156351E-04

## SAMPLE VARIANCE-COVARIANCE MATRIX

38396972E-14  
 .50921933E-15  
 .22052265E-13  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00

\*\*\*\*\* ANOVA AND F-EXP22 \*\*\*\*\*

SS = .65711140E-13 MEAN SQ = .82138925E-14  
 SS = .38324736E-12 MEAN SQ = .38324736E-12 F SAMPLE = 46.65843  
 DARD ERROR ESTIMATE = .96888109E-07

\*\*\*\*\*

## RESULTS OF REGRESSION FOR EXP23

ALPHA = .18077188E-04  
 BETA = .82699919E-05  
 GAMMA = .93736838E+00  
 AVG OF DEP VAR Y = .19188600E-04  
 ERR SUM SQUARES = .40159480E-12  
 AVG OF GAMMA POWER X = .13439253E+00

\*\*\*\*\*  
 INDEP VARIABLE DEPEND VARIABLE  
 TIME EXPTL FLUX

TIME	EXPTL FLUX	GAMA POWER X	YPRED
.1000000E+02	.22275600E-04	.52372459E+00	.22408334E-04
.2000000E+02	.20806900E-04	.27428744E+00	.20345516E-04
.3000000E+02	.19125500E-04	.14365107E+00	.19265167E-04
.3500000E+02	.18563000E-04	.10395858E+00	.18936915E-04
.6500000E+02	.18294000E-04	.14933376E-01	.18200689E-04
.7000000E+02	.18206000E-04	.10807387E-01	.18166564E-04
.9000000E+02	.18118900E-04	.29643304E-02	.19101703E-04
.1100000E+03	.18118900E-04	.81307858E-03	.18083912E-04

## SAMPLE VARIANCE-COVARIANCE MATRIX

.26340257E-13  
 .44121536E-13  
 .11289555E-11  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00

\*\*\*\*\* ANOVA AND F-EXP23 \*\*\*\*\*

ERR SS = .40159480E-12 MEAN SQ = .66932467E-13  
 REG SS = .16196554E-10 MEAN SQ = .16196554E-10 F SAMPLE = 241.98352  
 STANDARD ERROR ESTIMATE = .28340600E-06

\*\*\*\*\*

# RESULTS OF REGRESSION FOR EXP24

ALPHA= .22727380E-04  
 BETA= .59320638E-05  
 GAMMA= .97767533E+00  
 AVG OF DEP VAR Y= .25249300E-04  
 EPR SUM SQUARES= .17481767E-11  
 AVG OF GAMMA POWER X= .42513170E+00

INDEP VARIABLE	DEPEND VARIABLE	EXPTL FLUX	GAMA POWER X	YPRED
.10000000E+01	.28907000E-04	.28260100E-04	.97767533E+00	.28527027E-04
.50000000E+01	.28260100E-04	.26593100E-04	.89325053E+00	.28026214E-04
.10000000E+02	.25937300E-04	.25937300E-04	.79789650E+00	.27460567E-04
.30000000E+02	.24750700E-04	.24750700E-04	.50797198E+00	.25740714E-04
.40000000E+02	.24750700E-04	.24750700E-04	.40530899E+00	.25131710E-04
.60000000E+02	.24274700E-04	.24274700E-04	.25803544E+00	.24258073E-04
.65000000E+02	.24120100E-04	.24120100E-04	.23049029E+00	.24094674E-04
.70000000E+02	.23967400E-04	.23967400E-04	.20588557E+00	.23948717E-04
.80000000E+02	.23090600E-04	.23090600E-04	.16427538E+00	.23701882E-04
.90000000E+02	.23090600E-04	.23090600E-04	.13107475E+00	.23504934E-04
.10000000E+03	.23090600E-04	.23090600E-04	.10458408E+00	.23347789E-04

## SAMPLE VARIANCE-COVARIANCE MATRIX

.63175600E-12  
 .50618871E-12  
 .51155071E-12  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00

\*\*\*\*\* ANOVA AND F-EXP24 \*\*\*\*\*

R SS= .17481767E-11 MEAN SQ= .19424195E-12  
 G SS= .36660032E-10 MEAN SQ= .36660032E-10 F SAMPLE= 188.73395

ADAPD ERROR ESTIMATE= .46746346E-06

\*\*\*\*\*

# RESULTS OF REGRESSION FOR EXP25

ALPHA= .10507845E-04  
 BETA= .77130779E-05  
 GAMMA= .98800536E+00  
 AVG OF DEP VAR Y= .14272810E-04  
 EPR SUM SQUARES= .57377114E-12  
 AVG OF GAMMA POWER X= .48807054E+00

INDEP VARIABLE	DEPEND VARIABLE	EXPTL FLUX	GAMA POWER X	YPRED
.20000000E+02	.15844600E-04	.15844600E-04	.78557203E+00	.16567730E-04
.35000000E+02	.15381200E-04	.15381200E-04	.65550426E+00	.15564390E-04
.40000000E+02	.15208200E-04	.15208200E-04	.61712340E+00	.15268321E-04
.45000000E+02	.14621000E-04	.14621000E-04	.58098982E+00	.14989587E-04
.55000000E+02	.14025000E-04	.14025000E-04	.51494581E+00	.14480125E-04
.65000000E+02	.13524500E-04	.13524500E-04	.45640934E+00	.14078576E-04
.70000000E+02	.12793000E-04	.12793000E-04	.42968583E+00	.13822432E-04
.90000000E+02	.12539000E-04	.12539000E-04	.33754916E+00	.13111691E-04
.10500000E+03	.12539000E-04	.12539000E-04	.28166088E+00	.12680571E-04
.12500000E+03	.12539000E-04	.12539000E-04	.22126491E+00	.12214677E-04

## SAMPLE VARIANCE-COVARIANCE MATRIX

.18129114E-11  
 .11216021E-11  
 .84300211E-12  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00

\*\*\*\*\* ANOVA AND F-EXP25 \*\*\*\*\*

ERR SS= .57377114E-12 MEAN SQ= .71721392E-13  
 REG SS= .16864451E-10 MEAN SQ= .16864451E-10 F SAMPLE= 235.13837  
 STANDARD ERROR ESTIMATE= .28629933E-06

\*\*\*\*\*

## RESULTS OF REGRESSION FOR EXP26

ALPHA= .21071399E-04  
 BETA= .19261024E-05  
 GAMMA= .94140545E+00  
 AVG OF DEPEND VAR Y= .21456109E-04  
 EXP SUM SQUARES= .71121787E-12  
 AVG OF GAMMA POWER X= .19970912E+00

INDP VARIABLE	DEPEND VARIABLE	GAMA POWER X	YPRED
TIME	EXPTL FLUX	.94140545E+00	.22884915E-04
.10000000E+01	.22812400E-04	.54672266E+00	.22124597E-04
.10000000E+02	.22275600E-04	.40425054E+00	.21850138E-04
.15000000E+02	.21889300E-04	.16341849E+00	.21386190E-04
.30000000E+02	.21274400E-04	.48846712E-01	.21165487E-04
.50000000E+02	.20580700E-04	.36117599E-01	.21140966E-04
.55000000E+02	.21516200E-04	.26705604E-01	.21122835E-04
.60000000E+02	.21038100E-04	.14600558E-01	.21099516E-04
.70000000E+02	.21516200E-04	.79824559E-02	.21086767E-04
.80000000E+02	.21038100E-04	.43641895E-02	.21079796E-04
.90000000E+02	.21038100E-04	.23860012E-02	.21075985E-04
.10000000E+03	.21038100E-04		

## SAMPLE VARIANCE-COVARIANCE MATRIX

.19467982E-13  
 .90551373E-14  
 .10707509E-12  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00

\*\*\*\*\* ANOVA AND F-EXP26 \*\*\*\*\*

ERR SS= .71121787E-12 MEAN SQ= .79024207E-13  
 REG SS= .34930343E-11 MEAN SQ= .34930343E-11 F SAMPLE= 44.20208

STANDARD ERROR ESTIMATE= .29816477E-06

\*\*\*\*\*

## RESULTS OF REGRESSION FOR EXP27

ALPHA= .10298038E-04  
 BETA= .70555456E-05  
 GAMMA= .96022785E+00  
 AVG OF DEPEND VAR Y= .11299850E-04  
 EXP SUM SQUARES= .15343346E-12  
 AVG OF GAMMA POWER X= .14198933E+00

INDP VARIABLE	DEPEND VARIABLE	GAMA POWER X	YPRED
TIME	EXPTL FLUX	.96022785E+00	.13431443E-04
.20000000E+02	.13381100E-04	.19722953E+00	.11689600E-04
.40000000E+02	.11908300E-04	.16100650E+00	.11434027E-04
.45000000E+02	.11545300E-04	.13143617E+00	.11225392E-04
.50000000E+02	.11072600E-04	.87590679E-01	.10916038E-04
.60000000E+02	.10758100E-04	.58371503E-01	.10709881E-04
.70000000E+02	.10577800E-04	.38899485E-01	.10572495E-04
.80000000E+02	.10577800E-04	.17275468E-01	.10419926E-04
.10000000E+03	.10577800E-04		

## SAMPLE VARIANCE-COVARIANCE MATRIX

.38201812E-13  
 .10142202E-12  
 .84651698E-12  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00  
 .00000000E+00

\*\*\*\*\* ANOVA AND F-EXP27 \*\*\*\*\*

ERR SS= .15343346E-12 MEAN SQ= .25572244E-13  
 REG SS= .65178290E-11 MEAN SQ= .65178290E-11 F SAMPLE= 254.87904

STANDARD ERROR ESTIMATE= .17517618E-06

\*\*\*\*\*

# RESULTS OF REGRESSION FOR EXP28

```

CPHA= .83879685E-05
CTA= .54040594E-05
CMA= .97219723E+00
VG OF DEPEND VARIABLE= .10574306E-04
RR SUM SQUARES= .12745172E-11
VG OF GAMMA POWER X= .40457311E+00

*****
DEP VARIABLE      DEPEND VARIABLE      GAMMA POWER X      YPRED
TIME              EXPTL FLUX
10000000E+01      .97219723E+00      .13641780E-04
10000000E+02      .12215600E-04      .12464248E-04
20000000E+02      .12375600E-04      .11462704E-04
30000000E+02      .10460900E-04      .10707240E-04
40000000E+02      .10125200E-04      .10137393E-04
50000000E+02      .94671500E-05      .97075588E-05
60000000E+02      .89736000E-05      .93833347E-05
80000000E+02      .90526000E-05      .89542997E-05
10000000E+03      .89736000E-05      .87101927E-05

```

## SAMPLE VARIANCE-COVARIANCE MATRIX

```

.36540462E-12
.26703327E-12
.35887339E-12
.00000000E+00
.00000000E+00
.00000000E+00
.00000000E+00
.00000000E+00
.00000000E+00

```

\*\*\*\*\* ANOVA-AND F-EXP28 \*\*\*\*\*

```

SS= .12745172E-11      MEAN SQ= .18207389F-12
SS= .22248094E-10      MEAN SQ= .22248094E-10      F SAMPLE= 122.19266
DARD EPPOR ESTIMATE= .46088994E-06

```

\*\*\*\*\*